Theory of small-polaron band conduction in ultrapure organic crystals

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Abstract

We present a novel theory of charge-carrier mobilities in organic molecular crystals of high purity. Our approach is based on Holstein’s original concept of small-polaron bands but generalized with respect to the inclusion of nonlocal electron-phonon coupling. We derive an explicit expression for the mobilities as a function of temperature and, using \textit{ab-initio} methods to obtain the material parameters, we demonstrate its predictive power by applying it to naphthalene. The results show a remarkably good agreement with experiments and provide new insight into the difference between electron and hole mobilities as well as their peculiar algebraic and anisotropic temperature dependences.

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Organic semiconductors with \( \pi \)-conjugation are very promising materials for low-cost and easy-to-process electronic and optoelectronic devices such as light-emitting diodes [1,2], lasers [3,4], solar cells [5,6], and thin-film transistors [7–11]. Besides the polymeric materials, a very important class of organic semiconductors are molecular crystals of high purity. Due to their high degree of structural order, such crystals are ideal candidates for the investigation of the \textit{intrinsic} excitations and charge-carrier transport phenomena in organic solids. Consequently, many interesting fundamental experimental and theoretical studies have been performed in recent years and new results emerge at a rapid pace [12–16]. A particularly important and challenging topic is the understanding of the charge-carrier mobilities in these crystals, as the mobility is a fundamental material property and a central quantity for optimization of device performance.

In comparison to covalently bonded inorganic semiconductors, organic molecular crystals exhibit weak intermolecular bonds and, hence, narrower electron bands and stronger electron-lattice interaction. As a result, the dressing of the charge carriers by phonon clouds, i.e., polaron formation, becomes quite important. Pioneering theoretical work in this area was done by Holstein [17] who introduced the concept of small-polaron bands for a \textit{local} (on-site) electron-phonon coupling. The main prediction of his theory is that the mobilities initially decrease with rising temperature \( T \) due to bandwidth narrowing but increase again for higher \( T \) due to phonon-assisted hopping. Two decades after Holstein’s prediction, the interplay between metallic (bandlike) conduction and activated (hopping) transport in organic crystals was reported for the electrons in naphthalene but not for the holes [18–20]. Later, Kenkre \textit{et al.} were able to fit the measured electron mobilities reasonably well to Holstein’s model, assuming directionally-dependent local-coupling constants [21]. Despite the success of such a \textit{fitting} procedure, the lack of a first-principles description of charge-carrier mobilities in organic crystals has left several fundamental questions unanswered. This concerns, in particular, the different behavior of electrons and holes, the microscopic origin of the crystallographic anisotropy in the \( T \) dependence, and the influence of \textit{nonlocal} (Peierls-type) couplings such as present in the Su-Schrieffer-Heeger model [22]. Moreover,
the fundamental question has been raised whether or not the concept of small-polaron bands is applicable at all, since band motion may be washed out by even weak disorder [23].

In this Letter, we answer the above questions by developing a novel first-principles theory of charge-carrier mobilities in organic crystals. We present strong evidence for the usefulness of the small-polaron band picture once Holstein’s original model is extended towards the inclusion of nonlocal electron-phonon coupling. While a few theoretical studies on nonlocal coupling have been performed in the past [24–28], it was only recently that the importance of these contributions could be demonstrated explicitly in the case of polaron bandwidth narrowing in oligo-acene crystals [29]. Here, by means of the Kubo formalism, we obtain an explicit expression for the mobilities, including both local and nonlocal coupling. The practical usefulness of this approach is then exemplified by ab-initio studies for naphthalene (C$_{10}$H$_{8}$) crystals.

We consider a mixed Holstein-Peierls model for the interaction between electrons (holes) and phonons. In a tight-binding description, this corresponds to a Hamiltonian of the form $H = H_{el} + H_{ph} + H_{el- ph}$ where

$$H_{el} = \sum_{mn} \varepsilon_{mn} a_{m}^\dagger a_{n} ,$$

$$H_{ph} = \sum_{Q} \hbar \omega_{Q} (b_{Q}^\dagger b_{Q} + \frac{1}{2}) ,$$

$$H_{el- ph} = \sum_{mnQ} \hbar \omega_{Q} g_{mn} a_{m}^\dagger a_{n} (b_{Q}^\dagger + b_{-Q}) ,$$

describe the electrons, the phonons, and the electron-phonon interaction, respectively. Here, the operators $a_{m}^{(t)}$ and $b_{Q}^{(t)} := b_{Q\lambda}^{(t)}$ annihilate (create) an electron at equivalent lattice sites $R_{m} = \{R_{1}, \ldots , R_{N}\}$ with energy $\varepsilon_{mn}$ and a phonon in the mode $\lambda$ with wavevector $q$ and frequency $\omega_{\lambda q} =: \omega_{Q}$, respectively. The strength of the electron-lattice interaction in Eq. (3) is determined by the dimensionless quantities $g_{Qmn}$, which describe both the local coupling to the on-site energies $\varepsilon_{mn}$ (Holstein model) and the nonlocal coupling to the transfer integrals $\varepsilon_{mn}$ ($m \neq n$, Peierls model). The latter type of coupling will be shown to play a crucial role in the understanding of the anisotropic $T$ dependence of the mobilities.

For the description of the electrical conductivity, we use linear-response theory and intro-
duce a conductivity tensor \( \sigma_{\alpha\beta}(\omega) \) that relates the electric field \( E(\omega) \) present in the sample to the current \( J(\omega) \) that is induced by this field, \( J_\alpha(\omega) = \sum_\beta \sigma_{\alpha\beta}(\omega) E_\beta(\omega) \). Here, we concentrate on the mobilities \( \mu_\alpha \) which are obtained in the zero-frequency limit according to \( \sigma_{\alpha\alpha}(\omega \to 0) = N_c e_0 \mu_\alpha \), where \( e_0 \) equals the negative (positive) elementary charge in case of electron (hole) conduction and \( N_c \) denotes the number of charge carriers. In thermal equilibrium, the mobilities \( \mu_\alpha \) can be calculated by means of the Kubo formula for electrical conductivity \([30]\),

\[
\mu_\alpha = \frac{1}{2 N_c e_0 k_B T} \int_{-\infty}^{+\infty} dt \langle j_\alpha(t) j_\alpha(0) \rangle ,
\]

which relates the mobility to a microscopic current-current correlation function. The r.h.s. of Eq. (4) contains the quantum-mechanical current operator \( j(t) = e^{+iHt} j e^{-iHt} \) where \( j \) is obtained from the polarization operator \( P = e_0 \sum_m R_m a_m^\dagger a_m \) via the Heisenberg equation of motion \( j = \frac{dP}{dt} = \frac{i}{\hbar} [P, H] \). It is important to stress that the current \( j \) consists of two different contributions, \( j := j^{(I)} + j^{(II)} \), which are given by

\[
j^{(I)} = \frac{e_0}{i\hbar} \sum_{mn} (R_m - R_n) \varepsilon_{mn} a_m^\dagger a_n ,
\]

\[
j^{(II)} = \frac{e_0}{i\hbar} \sum_{mnQ} (R_m - R_n) \hbar \omega_Q g_{Qmn} (b_Q^\dagger + b_{-Q}) a_m^\dagger a_n ,
\]

and originate from \( H_{el} \) and \( H_{el-ph} \), respectively. While the current \( j^{(I)} \) contains only electron operators, the second term \( j^{(II)} \) describes a phonon-assisted current that stems solely from the nonlocal electron-phonon coupling and has no counterpart in local-coupling theories.

The evaluation of the Kubo formula (4) is performed by the method of canonical transformation \([30]\) within a generalized version that accounts for both local and nonlocal coupling \([27–29]\). By means of this technique, the electron-phonon interaction is incorporated non-perturbatively, in accordance with the underlying physical picture of small-polaron bands. Here, we skip the details of the quite tedious derivation and the approximations involved (which will be published elsewhere \([31]\)) but rather concentrate on the final results for the polaron mobilities in the case of dispersionless optical phonons \( (\omega_Q \to \omega_\lambda) \) for which symmetry requirements impose the form \( g_{Qmn} = \frac{1}{2\sqrt{N}} g_{\lambda mn} (e^{-iQ \cdot R_m} + e^{-iQ \cdot R_n}) \).
It is instructive to consider first the mobility $\mu^{(I)}_\alpha$ due to the currents $j^{(I)}$ in Eq. (5), which we obtain as

$$\mu^{(I)}_\alpha = \frac{e_0}{2k_BT \hbar^2} \sum_{n \neq m} (R_{n,m} - R_{m,n})^2 \int_{-\infty}^{+\infty} dt \left[ \varepsilon_{mn} e^{-\sum \lambda G_\lambda (1+2N_\lambda - \Phi_\lambda(t))} \right]^2 e^{-\Gamma^2 t^2},$$

(7)

where $N_\lambda = (e^{\hbar \omega_\lambda / k_BT} - 1)^{-1}$ denote the phonon occupation numbers. The extra factor involving the phenomenological broadening parameter $\Gamma$ accounts for scattering processes beyond the model, e.g., due to defects. Those terms in the exponent of Eq. (7) that contain the time-dependent auxiliary function $\Phi_\lambda(t) = (1+N_\lambda) e^{-i\omega_\lambda t} + N_\lambda e^{i\omega_\lambda t}$ describe incoherent scattering events involving actual changes in phonon numbers (hopping) whereas the remaining terms account for purely coherent scattering processes (bandwidth narrowing). While our above result for $\mu^{(I)}_\alpha$ can be compared to the Holstein-model mobilities obtained by Kenkre et al. [21,32], an important difference is that the exponent in our formula (7) is not only governed by the local coupling but by effective coupling constants $G_\lambda = (g_{\lambda mm})^2 + \frac{1}{2} \sum_{k \neq m,n} (g_{\lambda mk} g_{\lambda kn})^2$ that are composed of both the local and nonlocal ones.

So far, we have neglected the contributions from the phonon-assisted currents $j^{(II)}$ of Eq. (6). If we include them, we obtain the total mobilities $\mu_\alpha$ within the Holstein-Peierls model, which can be expressed in a form identical to Eq. (7) for $\mu^{(I)}_\alpha$, but with the replacement

$$(\varepsilon_{mn})^2 \rightarrow (\varepsilon_{mn} - \Delta_{mn})^2 + \frac{1}{2} \sum_\lambda (\hbar \omega_\lambda g_{\lambda mn})^2 \Phi_\lambda(t).$$

(8)

Here, we have introduced the shorthand notation

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

An essential qualitative difference between $\mu^{(I)}_\alpha$ and $\mu_\alpha$ is that only the total mobilities $\mu_\alpha$ can account for an anisotropic $T$ dependence. This is due to the additional terms containing $\Phi_\lambda(t)$ in Eq. (8), which describe incoherent scattering processes that are absent in local-coupling theories and reflect an inherently transport-promoting effect solely caused by the nonlocal coupling. The strength of the resulting phonon-assisted hopping and, hence, the anisotropy in the $T$ dependence is basically determined by the ratios $\hbar \omega_\lambda g_{\lambda mn} / \varepsilon_{mn}$, which may be dramatically different for different directions.
As a first application of the above theory, we perform model studies for naphthalene, which crystallizes in a monoclinic structure ($P2_1/\alpha$) and exhibits a herringbone stacking with two equivalent molecules per unit cell. In order to obtain the material-specific parameters $R_m, \varepsilon_{mn}, g_{\lambda mn}$, and $\omega_\lambda$ we use the following 3-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 [33]. For the lattice parameters we obtain the values $a = 7.68 \text{Å}$, $b = 5.76 \text{Å}$, $c = 8.35 \text{Å}$, and the monoclinic angle $\beta = 125.7^\circ$. For this geometry, the intermolecular optical-phonon energies ($\hbar\omega_1 = 10.7 \text{meV}$, $\hbar\omega_2 = 14.2 \text{meV}$, $\hbar\omega_3 = 17.4 \text{meV}$) and polarizations $e_\lambda$ are obtained within the rigid-molecule approximation, using a doubled Brillouin zone corresponding to the lattice $\{R_m\}$ of all the molecules [34]. In principle, our approach does also allow the inclusion of intramolecular phonons. However, in a recent Letter on oligo-acene molecules [12] it was reported that those intramolecular phonons that couple most strongly to the electrons have significantly higher frequencies than the intermolecular phonons considered here. Hence, while the zero-point fluctuations of the intramolecular phonons will lead to an isotropic overall reduction of the mobility values [35], their influence on the actual $T$ dependence will be small due to the low occupation of these modes up to room temperature.

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., $\{mn\} = \{0, a, b, c, ac, ab, abc\}$ belonging to $R_m - R_n = 0, \pm a, \pm b, \pm c, \pm (a+c), \pm (\frac{a+b}{2})$, and $\pm (\frac{a+b}{2} + c)$, respectively.

In the third step, we rotate the molecules by amplitudes $\Delta u_\lambda$ according to the polarizations $e_\lambda$ of phonon mode $\lambda$ (“frozen phonon”) and fit the new resulting *ab initio* band-structure again to the tight-binding model. Then, the electron-phonon coupling constants $g_{\lambda mn}$ are obtained from the changes in the transfer integrals by numerical differentiation.
\( g_{\lambda mn} = \frac{1}{\hbar \omega_{\lambda}} \frac{\Delta \varepsilon_{mn}}{\Delta u_{\lambda}} \), in the limit \( \Delta u_{\lambda} \to 0 \). All calculated parameters are compiled in Table I. Note that our calculated effective coupling constant \((g_{\text{eff}})^2 := \sum_{\lambda=1}^{3} G_{\lambda}=(1.52)^2\) for the LUMO band is comparable in value to the directionally-dependent fitted coupling values of 1.62, 1.83, and 1.88, as obtained by Kenkre et al. [21]. Finally, for the line broadening, we have chosen a small value of \( \hbar \Gamma = 0.1 \text{ meV} \), corresponding to the case of ultrapure crystals [36].

In Fig. 1, we present the electron and hole mobilities in naphthalene crystals as a function of temperature \( T \) for the \( a, b, \) and \( c' \) directions, with \( c' \) being perpendicular to the \( ab \)-plane of the molecular layers. We make three important observations. First, the hole mobilities are generally larger than the corresponding electron mobilities. Only in the \( a \) direction do we observe comparable mobilities for electrons and holes at \( T \approx 300 \text{ K} \). This general trend is in good agreement with experiments of Karl and co-workers [19,20]. Importantly, the lower electron mobilities cannot be understood by simply looking at the transfer integrals of Table I but they are mainly due to their stronger coupling to the phonons (LUMO: \( g_{\text{eff}} = 1.52 \), HOMO: \( g_{\text{eff}} = 0.92 \)).

Second, while the hole mobilities in the different directions decrease very similarly with \( T \), the electron mobilities exhibit a pronounced anisotropic \( T \) dependence. In particular, we find a metallic (bandlike) behavior within the \( ab \)-plane and a slightly activated (hopping) transport in the \( c' \) direction. Again, these findings from our \textit{ab initio} calculations are in good agreement with experimental data [18,19], which show such a nearly \( T \)-independent mobility around \( T \approx 150 \text{ K} \) exclusively in the \( c' \) direction. As discussed above, this pronounced anisotropy is due to the phonon-assisted currents \( j^{(II)} \) and depends on the ratios \( \hbar \omega_{\lambda} g_{\lambda mn}/\varepsilon_{mn} \). For the electrons, this ratio is particularly high for \( \hbar \omega_{2g_{2e}}/\varepsilon_{c} \), which explains the peculiar flattening of \( \mu_{c'} \) that is not seen at all for \( \mu_{c'}^{(I)} \) alone. Thus, our findings show clearly that anisotropy effects in the \( T \) dependence can be explained in a natural way by the inclusion of nonlocal electron-phonon coupling, and do not require the use of additional concepts such as a directionally-dependent local couplings [21] or correlated successive hops.
of strongly localized charge carriers [37].

Third, our calculated hole mobilities obey at elevated temperatures the power law
\( \mu_\alpha \propto T^{-2.5} \). This agrees nicely with Karl’s experiments [19] who found \( \mu_\alpha \propto T^{-\gamma} \) (\( \gamma = 2.9, 2.5, 2.8 \)). This peculiar power-law dependence, which has been poorly understood so far and for which several explanations have been put forward [20], can be straightforwardly understood from our theory. In the limit of small broadening \( h\Gamma \) and for \( \mu_\alpha \approx \mu_\alpha^{(I)} \) (here fulfilled for the holes), a spectral analysis of Eq. (7) shows that the dominant electron-phonon scattering processes are those that allow only energy exchange within each phonon mode but not between different modes, and the mobility can be expressed in terms of modified Bessel functions,
\[
\mu_\alpha^{(I)} \propto \frac{1}{1 - k_B T} \left( \prod_{\lambda=1}^3 e^{-2G_\lambda(1+2N_\lambda)}I_0(z_\lambda) \right),
\]
where \( z_\lambda = 4G_\lambda \sqrt{N_\lambda(1+N_\lambda)} \). The limit of high \( T \) is obtained using \( I_0(z_\lambda \to \infty) \approx e^{z_\lambda}/\sqrt{2\pi z_\lambda} \) and we find \( \mu_\alpha^{(I)} \propto T^{-1} \left( \prod_{\lambda=1}^3 T^{-0.5} \right) = T^{-2.5} \) which indicates that the exponent is actually a measure for the number of relevant phonon modes per molecule. For the electrons, the situation is more complicated due to a subtle interplay between the now significant contributions of \( j^{(II)} \) and the larger \( g_{\text{eff}} \) value. This prohibits an easy analytical evaluation but, by looking at our calculated in-plane electron mobilities in Fig. 1, we find at high \( T \) an approximate \( T^{-1.5} \) dependence, again in close agreement with the experimental observations [19,20].

In summary, we have presented a novel theoretical description of charge-carrier mobilities in ultrapure organic crystals based on a mixed Holstein-Peierls model where not only the local but, importantly, also the nonlocal electron-phonon coupling is included. The predictive power of our theory and the usefulness of the small-polaron band concept have been demonstrated by \textit{ab initio} studies for naphthalene crystals where our results show a remarkably good agreement with experiments and provide new microscopic insight into several hitherto poorly understood phenomena including the different behavior of electrons and holes as well as the peculiar algebraic and anisotropic temperature dependences. Finally, since our theory may also be applied to other weakly-bonded materials with strong electron-phonon coupling, it may become an important contribution to the understanding of the intrinsic charge-carrier transport in these materials, too.
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Brillouin-zone center.

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[36] We have carefully checked that, for the temperature region shown in Fig. 1, smaller values of $\hbar \Gamma$ do not change the actual $T$ dependence of the mobilities but lead only to a scaling $\propto 1/\Gamma$ of their overall values.

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### TABLE I

| \( \{mn\} \) | \( \varepsilon_{mn} \) (meV) | \( g_{1mn} \) | \( g_{2mn} \) | \( g_{3mn} \) | \( \varepsilon_{mn} \) (meV) | \( g_{1mn} \) | \( g_{2mn} \) | \( g_{3mn} \) |
|---------------|----------|----------|----------|----------|----------|----------|----------|----------|
| 0             |         | -0.04   | 0.33     | 0.33     | -0.08    | 0.09     | 0.05     |
| a             | -29     | -0.03   | -0.24    | 0.01     | 1        | 0.03     | -0.05    | 0.01     |
| b             | -59     | 0.43    | 0.05     | 0.20     | 30       | -0.87    | 0.09     | 0.00     |
| c             | 4       | 0.01    | 0.09     | 0.02     | 1        | -0.15    | 0.53     | -0.05    |
| ac            | 6       | -0.02   | 0.00     | -0.05    | -3       | 0.07     | -0.18    | -0.01    |
| ab            | 17      | -0.25   | -0.25    | 0.05     | -72      | 0.11     | -0.69    | -0.11    |
| abc           | -24     | 0.15    | 0.08     | -0.06    | -4       | -0.08    | 0.28     | -0.08    |

\( g_{\text{eff}} \) \( G_1 \) \( G_2 \) \( G_3 \)

| \( g_{\text{eff}} \) | \( G_1 \) | \( G_2 \) | \( G_3 \) | \( g_{\text{eff}} \) | \( G_1 \) | \( G_2 \) | \( G_3 \) |
|----------------------|----------|----------|----------|----------------------|----------|----------|----------|
| 0.92                 | 0.36     | 0.32     | 0.16     | 1.52                 | 0.83     | 1.44     | 0.04     |

**TABLE I.** Top: transfer integrals \( \varepsilon_{mn} \) and electron-phonon coupling constants \( g_{\lambda mn} \) for the HOMO and LUMO bands of naphthalene crystals. Bottom: effective coupling constants \( (g_{\text{eff}})^2 = \sum_{\lambda=1}^{3} G_\lambda \), where \( G_\lambda = g_{\lambda 0}^2 + g_{\lambda a}^2 + g_{\lambda b}^2 + g_{\lambda c}^2 + g_{\lambda ac}^2 + 2g_{\lambda ab}^2 + 2g_{\lambda abc}^2 \).
FIGURES

FIG. 1. Charge-carrier mobilities vs temperature $T$ for the $a$, $b$, and $c'$ directions in naphthalene crystals. Top 3 curves: $\mu_a$ for holes, middle 3 curves: $\mu_a$ for electrons, bottom curve: $\mu_{c'}^{(f)}$ for electrons. As a guide to the eye, several power laws $\mu_a \propto T^{-\gamma}$ are also depicted. All mobilities are plotted in units of $\frac{cm^2}{Vs} \times \frac{76\text{meV}}{\hbar}$ but an unknown prefactor $r$ [35] should be included.
Mobility vs. Temperature (Kelvin)

- $\gamma = 2.5$
- $\gamma = 2.0$
- $\gamma = 1.5$
- $\gamma = 1.0$

- electrons
  - $\mu_a$
  - $\mu_b$
  - $\mu_c$

- holes
  - $\mu_a$
  - $\mu_b$
  - $\mu_c'$

- $\mu_c^{(1)}$