Charge transport in organic crystals: interplay of band transport, hopping and electron–phonon scattering

Frank Ortmann\textsuperscript{1,2,3,4}, Friedhelm Bechstedt\textsuperscript{1,2} and Karsten Hannewald\textsuperscript{1,2}

\textsuperscript{1} Institut für Festkörpertheorie und -optik, Friedrich-Schiller-Universität Jena, Germany
\textsuperscript{2} European Theoretical Spectroscopy Facility, Max-Wien-Platz 1, 07743 Jena, Germany
E-mail: ortmann.f@googlemail.com

\textit{New Journal of Physics} \textbf{12} (2010) 023011 (7pp)
Received 23 September 2009
Published 10 February 2010
Online at \url{http://www.njp.org/}
doi:10.1088/1367-2630/12/2/023011

\textbf{Abstract}. We present an \textit{ab initio} description of charge transport in organic semiconductors based on a recently developed theory that goes beyond small-polaron and/or narrow-band models. The mobility expression is evaluated with parameters from density functional theory, and application to naphthalene crystals demonstrates substantial progress in the simulated temperature dependence and relative magnitudes for all transport directions. The scattering by phonons is described in a manner that goes beyond the Holstein model for small polarons and, consequently, significantly improves the temperature dependence and anisotropy of carrier mobility with respect to the previous narrow-band theory. The contributions of coherent and incoherent scattering processes are analyzed. Special emphasis is placed on the origin and understanding of the transition from band transport at low temperatures to hopping at high temperatures, both of which are fully included in the theory. Additionally, in contrast to earlier narrow-band theories, the unphysical divergence at zero temperatures is removed.

Theories of charge transport in semiconductors are commonly based on one of two major paradigms: either coherent band transport or incoherent hopping transport. In the past, discussions on whether a band-transport theory or a hopping theory should be applied to

\textsuperscript{3} Present address: INAC/SPrAM/GT, CEA Grenoble, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France.
\textsuperscript{4} Author to whom any correspondence should be addressed.
the particular crystal under study arose from the complicated interplay of several key energy scales [1], such as bandwidth $B$, temperature $k_B T$, polaron binding energy [2] or other scattering energies $\hbar / \tau$ with relaxation time $\tau$. For many systems, such as organic semiconductors, this decision is not easily made. In particular for organic single crystals, which have attracted intense experimental interest [3]–[9], a recent review states that the ‘understanding of charge transport . . . remains limited’ [5]. In fact, bare electronic bandwidths of organic molecular crystals can reach 700 meV [10] or even more [11], but are strongly reduced by scattering [12] and polaronic effects [13], thus implying that both types of transport are important [14, 15].

An illuminating prototypical example for studies of the two transport limits is crystalline naphthalene. High mobilities at low $T$ and power-law-like $T$-dependencies have been interpreted as clear indications for band transport [16]. On the other hand, the temperature independence of electron mobility in the $c^*$-direction at high $T$ can only be explained by hopping theories where thermally activated processes are considered. The restriction to either theory appears inadmissible, but the linkage of both is still not fully understood [14, 15]. An important milestone in merging both approaches was the introduction of the polaron concept [2], because the resulting theories, which are based on the so-called narrow-band approximation (NBA), were able to explain decreasing mobilities for increasing temperatures [17, 18]. First-principles calculations combined with the polaron concept could even explain the difference between electron and hole transport in naphthalene, including the nearly constant electron $c^*$-mobilities at elevated $T$ [19].

Until recently, mobility theories were successfully applied down to several tens of kelvin, but with a resulting unphysical divergence in the limit $T \rightarrow 0$ [17, 18, 20, 21]. This striking discrepancy between theory and experiment was mentioned previously by Kenkre when collecting some important arguments about this low-$T$ limit and the corresponding relation between band transport and hopping [14]. However, it was only recently that a theory, which unifies both concepts in a natural way, was derived by the authors [22]. This generalized theory is able to describe all relevant limits, including the smooth transition from hopping to band transport with decreasing temperature and the removal of the low-$T$ singularity. As a result, it is applicable to materials with arbitrary bandwidths and up to arbitrarily low temperatures.

Here, we present a first application of this theory of charge transport in organic crystals. We show that the theory can be easily supplemented by modern ab initio calculations for all necessary material parameters. As a prototypical example, we apply this theory to naphthalene crystals and calculate the $T$ dependence and anisotropy of the hole mobilities.

For the present paper, we briefly review the major characteristics of the approach derived in [22]. The charge-carrier mobility is calculated from the Kubo formalism for the conductivity, which describes the linear current response to an applied electric field. The dc-mobility tensor of the charge carriers can be written in terms of the current–current correlation function [23]

$$\mu_{\alpha\beta} = \frac{1}{e_0 N_c} \frac{1}{2 k_B T} \int_{-\infty}^{\infty} dt \langle j_\alpha(t) j_\beta(0) \rangle_H. \quad (1)$$

$N_c$ is the number of carriers and the brackets $\langle \rangle_H$ denote the statistical average over electron and phonon degrees of freedom of the system with the Hamiltonian

$$H = \sum_{MN} \epsilon_{MN} \hat{a}_M^\dagger \hat{a}_N + \sum_Q \hbar \omega_Q \left( \hat{b}_Q^\dagger \hat{b}_Q + \frac{1}{2} \right) + \sum_{MQ} \hbar \omega_Q S_{MM}^Q \left( \hat{b}_Q^\dagger + \hat{b}_-Q \right) a_M^\dagger a_M. \quad (2)$$
Here, a site representation of annihilation (creation) operators $a_M$ ($a_M^\dagger$) for electrons at sites $R_M$ is chosen. Importantly, the off-diagonal transfer integrals $\varepsilon_{MN}$ give rise to both the $k$-dispersion of the corresponding conduction (or valence) band and non-vanishing current operators $j_a = (e_0/i\hbar) \sum_{MN} (R_{Ma} - R_{Na}) \varepsilon_{MN} a_M^\dagger a_N$. For the phonons, annihilated (created) by $b_Q^\dagger$ ($b_Q$), $\omega_Q \equiv \omega_\lambda(q)$ gives the frequency of the mode $\lambda$ at wavevector $q$. The interaction of particles with vibrations is mediated by the dimensionless electron–phonon coupling constants $g_{\lambda MN}^Q \equiv g_{\lambda MN}(q)$, i.e. the local coupling according to the Holstein Hamiltonian [2]. In order to account for the coupling effects in all orders, the transition into the polaron picture is performed by a canonical transformation [23] that allows one to write

$$\mu_{\alpha\beta} = \frac{1}{e_0 N_c} \frac{1}{2 k_B T} \int_{-\infty}^{\infty} dt \langle \tilde{j}_\alpha(t) \tilde{j}_\beta(0) \rangle \tilde{H}. \tag{3}$$

The statistical average in (3) must then be calculated with the transformed operator $\tilde{H}$, which, in general, cannot be done exactly [22]. However, it can be performed with the approximate Hamiltonian

$$\tilde{H} = \sum_k \tilde{\varepsilon}(k) a_k^\dagger a_k + \sum_Q \tilde{h}_Q \left( b_Q^\dagger b_Q + \frac{1}{2} \right) \tag{4}$$

instead, where $\tilde{\varepsilon}(k)$ is the temperature-dependent polaron band energy. It has been discussed in [22] that such an approach has been used previously in the literature (see also Mahan’s textbook [23]), but only in connection to the NBA. These earlier works assume that the polaron bandwidth $\tilde{B}$ is zero, i.e. $\tilde{\varepsilon}(k) \to$ const, which effectively limited their validity range to the high-$T$ regime ($k_B T > \tilde{B}$). However, since this approximation turned out to be unnecessary in this step, it has been dropped in [22], which strongly extends the validity range of the final mobility expression presented below. In particular, the limitations to the high-$T$ regime no longer exist with the full $T$-dependent bandwidth taken into account in the polaron band energy $\tilde{\varepsilon}(k)$ in (4). In this way, the band dispersion and related band occupation effects (Pauli blocking) are included. Hence, the derivation in [22] for arbitrary bandwidths has been identified as the reason why the present theory should perform much better than previous approaches.

We finally give the result obtained in [22] for the mobility tensor

$$\mu_{\alpha\beta} = -\frac{1}{e_0 N_c} \frac{1}{2 k_B T} \left( \frac{e_0}{\hbar} \right)^2 \sum_{LMN} R_{L\alpha} \tilde{\varepsilon}_{0L} R_{N\beta} \tilde{\varepsilon}_{0N}$$

$$\times \frac{1}{N_c^2} \sum_{k_1 k_2} e^{-i k_1 (R_{L\alpha} + R_N)} e^{i k_2 (R_{L\alpha} - R_N)} n_{k_1} (1 - n_{k_2})$$

$$\times \int_{-\infty}^{\infty} dt e^{\frac{\mu}{\hbar} [\tilde{\varepsilon}(k_1) - \tilde{\varepsilon}(k_2)]} e^{-\sum_{\phi}(\Phi_\lambda(q,t)G_{\phi 1\phi 0}(q) e^{iB_M})}, \tag{5}$$

where the abbreviations

$$\Phi_\lambda(q,t) = N_\lambda(q) e^{i\omega_\lambda(q)t} + \left[ 1 + N_\lambda(q) \right] e^{-i\omega_\lambda(q)t},$$

$$G_{\phi 0\phi N}(q) = \left[ g_{\phi 0\phi}(q) - g_{\phi L\phi}(q) \right] \left[ g_{\phi 0\phi}(-q) - g_{\phi N\phi}(-q) \right]$$

$^5$ For convenience, we use only the term electron throughout the paper although it also applies to holes. It is clear that there is no difference in treating electrons and holes with this formalism.

New Journal of Physics 12 (2010) 023011 (http://www.njp.org/)
have been introduced. \( n_{k_i} = (1 + \exp[(\varepsilon(k_i) - \zeta)/k_BT])^{-1} \) is the Fermi–Dirac distribution with the chemical potential \( \zeta = \zeta(T, N_{\Omega}) \). \( N_{\Omega} \) denotes the number of unit cells in the sample volume \( \Omega \). Expression (5) contains various physically important effects, e.g. anisotropy effects due to crystal geometry and band structure (first line), Pauli blocking of charge carriers (second line), and energy and momentum conservation in all possible scattering events (second and third lines). In addition, a collision time \( \tau \) (non-phonon scattering) may be introduced by means of the replacement \( \int dt \to \int dt \, e^{-(t/\tau)^2} \), as suggested in the literature [18]. The parameter \( \tau \) takes additional scattering processes that are beyond the couplings to the phonon bath into account. In particular, it simulates the purity and crystallinity of a sample.

Although (5) is the primary result of [22], we proceed with an illustrative transformation. Coherent and incoherent contributions to the mobility are identified in (5) from the exponential series of the last term in the third line. This series may be regarded as a series in the coupling parameter \( G_{\text{LOON}}^\beta(q) \), which is a result of the non-perturbative treatment of electron–phonon interaction. The exponential may be separated into an absolute term (zeroth order of \( G_{\text{LOON}}^\beta(q) \)) and a remaining term (higher powers of \( G_{\text{LOON}}^\beta(q) \)), which are identified as coherent and incoherent mobility contributions, respectively. According to these two qualitatively different contributions, the mobility is split into two parts: \( \mu_{\alpha\beta} = \mu_{\alpha\beta}^{(\text{coh})} + \mu_{\alpha\beta}^{(\text{inc})} \). The coherent part, which plays a crucial role for low \( T \), can be rewritten as

\[
\mu_{\alpha\beta}^{(\text{coh})} = \frac{\sqrt{\pi} \epsilon_{0} \tau}{2N_{\Omega}e k_{B}T} \sum_{k_{1}} n_{k_{j}} \left(1 - n_{k_{j}}\right) \tilde{v}_\alpha(k_{j}) \tilde{v}_\beta(k_{j}),
\]

where \( \tilde{v}_\alpha(k) = \frac{1}{\hbar} (\partial \varepsilon(k)/\partial \varepsilon_{\alpha}) \) is the polaron band velocity. The appearance of the band velocity derives from the fact that the charge carriers move coherently through the crystal.

Expression (6) resembles the textbook formula of the band mobility as derived from the Boltzmann equation [24]. Importantly, however, the result also includes the (potentially strong) polaron renormalization \( (v \to \tilde{v}) \), which arises in a natural way from the inclusion of electron–phonon coupling.

The above-developed theory is applied to crystalline naphthalene. We restrict ourselves to the simulation of hole mobilities, as for the electrons it has been shown that contributions from non-local electron–phonon interaction (which is beyond the Holstein Hamiltonian for electron–phonon coupling) are important for at least one direction \( (c^\ast) \) [19]. All necessary material parameters have been determined by ab initio calculations (see table III in [13]). We use the values of \( a = 7.68 \, \text{Å}, b = 5.76 \, \text{Å}, c = 8.35 \, \text{Å} \) and \( b = 125.7^\circ \) for the monoclinic lattice, three intermolecular phonons of Einstein type as scatterers with energies of \( h\omega_\lambda = 10.7, 14.2 \) and \( 17.4 \, \text{meV} \), and effective coupling constants \( g_\lambda^2 = 0.36, 0.32 \) and 0.16, respectively, where \( g_{\lambda M\mu}^\ast(q) = (g^\ast/\sqrt{N_{\Omega}})e^{i\mathbf{qR}} \) is used to model the wavevector dependence of the coupling. The transfer integrals amount to \( \varepsilon_a = -29, \varepsilon_b = -59, \varepsilon_c = 4, \varepsilon_{ab} = 17, \varepsilon_{ac} = 6 \) and \( \varepsilon_{abc} = -24 \, \text{meV} \). In accordance with previous calculations, we choose \( \hbar/\tau = 0.1 \, \text{meV} \) for ultrapure crystals and assume a low carrier concentration of \( N_c/N_{\Omega} = 10^{-8} \).

The numerical results are plotted in figure 1 in comparison to experimental data [25] and mobilities as obtained within the NBA. All graphs show hole mobilities along the crystallographic directions \( a, b \) and \( c^\ast \) (perpendicular to \( a \) and \( b \)). The \( ab \) plane is the herringbone stacking plane of the naphthalene crystal.

The figures show several important features. Firstly, within the present theory, the mobilities for the low-\( T \) regime are finite. In contrast to the narrow-band theory, which suffers from a divergence in this limit, the mobilities exhibit the same plateau-like behaviour as in the

\* New Journal of Physics 12 (2010) 023011 (http://www.njp.org/)
Figure 1. Anisotropy and temperature dependence of naphthalene hole mobilities from (5) (left) and within the NBA [19] (right) compared to experimental data [25] (middle). Lines in the experimental data are guides to the eye. In $a$ and $c^*$ direction, the upper experimental curve corresponds best to the low-field limit (see text). Resolution according to $\mu_{\alpha\beta} = \mu_{\alpha\beta}^{(coh)} + \mu_{\alpha\beta}^{(inc)}$ is given as dashed and dotted lines, respectively.

Experimental curves. This is traced back to the improved low-$T$ treatment in the present theory, which correctly describes that the current, and hence the mobility, originates from polarons in a thermal layer of width $\propto k_B T$ at the chemical potential, as evident from the Pauli-blocking factor $n_{k_\perp}(1 - n_{k_\perp})$ in (6). As a consequence, the $T^{-1}$ dependence from the prefactor is cancelled and $\mu_{\alpha\beta}^{(coh)}$ and $\mu_{\alpha\beta}^{(inc)}$ become finite in the $T \to 0$ limit. This significant improvement over previous theories of charge transport in organic crystals is expected since the bandwidth is no longer restricted to energies smaller than $k_B T$ as in the narrow-band theory.

Secondly, the calculated mobilities show an improved direction dependence, as is obvious by comparison with the measured mobility anisotropy. The highest mobilities are observed within the herringbone plane, which is in accordance with the picture of strongest overlap of molecular orbitals [26, 27]. Also the experiments find very similar mobilities in the $a$- and $b$-direction. Note that the calculated mobilities in the $a$ ($c^*$-)direction should be compared to the upper black (green) experimental curve at low $T$ for which hot-carrier effects are reduced. Unfortunately, some data points for highest mobilities at 4 K were not reported, but the existence of a small plateau is evident from all the data in the reference.

Thirdly, the calculated mobilities exhibit the same temperature evolution above 100 K, as found in the experiments. They are best represented by a power-law dependence $T^{-\gamma}$ with $\gamma$ values of 3.3, 3.1 and 2.7, which is relatively close to the values obtained in the measurements, where power-law fits yield exponents of $\gamma = 2.9$, 2.5 and 2.8 in the $a$-, $b$- and $c^*$-direction, respectively. The agreement between the new approach and the experiment, however, is not

$^6$ Power-law behavior was observed in the temperature range of 120–300, 120–300 and 160–300 K for the directions $a$, $b$ and $c^*$, respectively. The fits have been carried out on these intervals.
perfect. The length of the plateau is somewhat overestimated, which might be due to the neglect of low-energy acoustic phonons. These have not been studied in this paper because the role of these phonons has not yet been established in the literature [28]. At high $T$, the theoretical values of $\mu_a$ and $\mu_c$ are closer to each other than in the experiment. This effect was already observed within the NBA and indicates that the narrow-band theory is the high-$T$ limit of the more general theory used here.

In order to get a deeper understanding of the transport mechanism, we split the mobility along the $a$-direction into two contributions, as discussed above. The coherent part $\mu_{a\beta}^{(coh)}$ is calculated from (6) and displayed as a dashed line in figure 1. It dominates the total mobility at low temperatures, but a rapid transition to predominantly hopping motion $[\mu_{a\beta}^{(inc)}]$ is observed at elevated $T$. This transition is restricted to an interval of a few tens of kelvin and gives valuable insight into the problem of an $a$ priori assignment to either transport regime. Clearly, both contributions are required for a comprehensive description.

In conclusion, we have shown that the recently derived formula for the mobility of charge carriers in semiconductors, which is applicable to wide-band and narrow-band crystals, can be used along with state-of-the-art density functional theory computations for material parameters of organic crystals. As a prototypical example, it has been demonstrated that the novel approach gives a better description of the transport properties for holes in naphthalene crystals. This includes the description of the temperature dependence and the direction dependence of the mobilities which match much better with experimental curves. Due to the correct statistical description of the charge carriers, the low-$T$ mobility limit is obtained correctly. On the other hand the results cover the previous narrow-band mobilities for high $T$. Finally, we analyzed the transport mechanism for these crystals and found that band transport dominates in the low-$T$ regime, while at room temperature hopping is the prevailing transport mechanism.

Acknowledgments

We thank the Deutsche Forschungsgemeinschaft (Project No. HA 2900/3-2,3) for financial support. This work was supported by the European Community within the NANOQUANTA Network of Excellence (Contract No. NMP4-CT-2004-500198). Grants for computer time from the Leibniz-Rechenzentrum München are gratefully acknowledged.

References

[1] Brédas J-L, Calbert J P, da Silva Filho D A and Cornil J 2002 Proc. Natl Acad. Sci. USA 99 5804
[2] Holstein T 1959 Ann. Phys. 8 325
[3] Jurchescu O D, Baas J and Palstra T T M 2004 Appl. Phys. Lett. 84 3061
[4] Sundar V C, Zaumseil J, Podzorov V, Menard E, Willett R L, Someya T, Gershenson M E and Rogers J A 2004 Science 303 1644
[5] Gershenson M E, Podzorov V and Morpurgo A F 2006 Rev. Mod. Phys. 78 973
[6] Hulea I N, Fratini S, Xie H, Mulder C L, Iossad N N, Rastelli G, Ciuchi S and Morpurgo A F 2006 Nat. Mater. 5 982
[7] Tripathi A K and Pflaum J 2006 Appl. Phys. Lett. 89 082103
[8] Koch N, Vollmer A, Salzmann I, Nickel B, Weiss H and Rabe J P 2006 Phys. Rev. Lett. 96 156803
[9] Chi X, Li D, Zhang H, Chen Y, Garcia V, Garcia C and Siegrist T 2008 Org. Electron. 9 234
[10] Koller G, Berkebile S, Oehzelt M, Puschning P, Ambrosch-Draxl C, Netzer F P and Ramsey M G 2007 Science 317 351

New Journal of Physics 12 (2010) 023011 (http://www.njp.org/)
[11] Ortmann F, Hannewald K and Bechstedt F 2007 Phys. Rev. B 75 195219
[12] Troisi A and Orlandi G 2006 Phys. Rev. Lett. 96 086601
[13] Hannewald K, Stojanović V M, Schellekens J M T, Bobbert P A, Kresse G and Hafner J 2004 Phys. Rev. B 69 075211
[14] Kenkre V M 2002 Phys. Lett. A 305 443
[15] Cheng Y C and Silbey R J 2008 J. Chem. Phys. 128 114713
[16] Warta W and Karl N 1985 Phys. Rev. B 32 1172
[17] Kenkre V M, Andersen J D, Dunlap D H and Duke C B 1989 Phys. Rev. Lett. 62 1165
[18] Hannewald K and Bobbert P A 2004 Phys. Rev. B 69 075212
[19] Hannewald K and Bobbert P A 2004 Appl. Phys. Lett. 85 1535
[20] Silbey R J and Munn R W 1980 J. Chem. Phys. 72 2763
[21] Fratini S and Ciuchi S 2003 Phys. Rev. Lett. 91 256403
[22] Ortmann F, Bechstedt F and Hannewald K 2009 Phys. Rev. B 79 235206
[23] Mahan G D 2000 Many-Particle Physics (New York: Kluwer)
[24] Ziman J M 2001 Electrons and Phonons (Oxford: Clarendon)
[25] Karl N 1985 Organic Semiconductors Landolt–Börnstein Numerical Data and Functional Relationships in Science and Technology (New Series), vol 17i Group III ed O Madelung, M Schulz and H Weiss (Berlin: Springer) pp 106–218
[26] Ortmann F, Hannewald K and Bechstedt F 2008 Appl. Phys. Lett. 93 222105
[27] Ortmann F, Hannewald K and Bechstedt F 2009 J. Phys. Chem. B 113 7367
[28] Coropceanu V, Cornil J, da Silva Filho D A, Olivier Y, Silbey R and Brédas J-L 2007 Chem. Rev. 107 926

New Journal of Physics 12 (2010) 023011 (http://www.njp.org/)