Field-dependent Transport Level and Mobility in Disordered Organics

V.R. Nikitenko*, N.A. Sannikova, M.N. Strikhanov

*National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Kashirskoe highway, 31, Moscow, 115409, Russia

Abstract

An analytic description of electric field and temperature dependences of mobility is developed on the base of extended transport level concept in the framework of Gaussian disorder model, providing low concentration of charge carriers. Field-dependent percolation factor was used in an equation for transport level. Results are in good agreement with well-known Monte Carlo simulations at weak and moderate electric field strength (up to 106 V/cm at typical parameters), providing that energetically upward jumps still dominate conductivity. It is enough for most applications in organic electronics. Concentration dependence of a transport level is discussed.

Keywords: disordered organics, transport level; mobility

1. Introduction

Charge transport properties are decisive in operating of devices, hence correct theoretical description of charge transport is a matter of major importance. Simple phenomenological models, at first – the Gaussian disorder model (GDM) by Bässler (1993) forms a basis of theoretical description and modeling of charge transport in disordered

* Corresponding author. Tel.: +8-495-788-5699.
E-mail address: vmikitenko@mephi.ru
organic semiconductors. The basic charge transport mechanism in disordered organics is incoherent hopping of carriers between localized states. In agreement with GDM, these states are randomly distributed in energy, following the Gaussian distribution, \( g(E) = \left( \frac{1}{\sqrt{2\pi}\sigma} \right) \exp\left[ -E^2/(2\sigma^2) \right] \), where \( \sigma \) is the variance of this distribution of states (DOS). A powerful analytic tool in the framework of GDM is a concept of transport level (transport energy), which allows to employ a relatively simple formalism of multiple trapping model to description of hopping transport, see the works by Nikitenko and Strikhanov (2014) and Bässler et al. (2007). This concept, however, has been applied previously only to the calculations of mobility in the limit of weak electric field, for example, by Nikitenko and Strikhanov (2014), Bässler et al. (2007), Baranovskii et al. (2000), Baranovskii et al. (2002), Arkhipov et al. (2001).

We propose an analytic model of field-dependent transport level and discuss its applicability to the modeling of field and temperature dependence of mobility in organic disordered semiconductors, providing low concentrations of charge carriers. This case is suitable for organic light-emitting diodes.

2. Theory

In accord with the transport level concept, carriers jump to states, whose energies lie in a band near some energy \( E_{\text{trans}} \) (real transport level), from deeper localized states, see Nikitenko and Strikhanov (2014), Baranovskii et al. (2000), Baranovskii et al. (2002).

The electric field changes the energy of all the states by addition of electrostatic term, \( eFr \cos(\theta) \), where \( r \) is hopping distance, \( F \) is the electric field strength, and \( \theta \) is the angle between the hopping direction and the direction of electric force. Electrons jump against the field \( F \), the average activation energy will decrease. Formally, this can be represented as a decreasing the transport energy with increasing field, providing that energetically upward jumps still dominates transport.

\[ E_{\text{trans}}(x) = E_{\text{max}}(0) - xeFr \cos(\theta), \quad x = r \cos(\theta), \quad \theta = 0 \text{ (the right side)}, \quad \theta = \pi \text{ (the left side)}. \]

Vertical and horizontal strokes respond to thermally activated and non-activated hopping, respectively.

Formal (effective) transport level, \( E_{\text{tr}} \), is defined by Nikitenko and Strikhanov (2014) and Arkhipov et al. (2001) of the reasons that a certain number of states, \( B \), should be inside the certain area of \( E-r \) space, which is available for the jump. The boundary of this region is determined by the condition that the hopping rate \( \nu \) from an initial state of the energy \( E \) to any state of the energy \( E' \) inside this area exceeds a certain value, \( \nu > \nu_0 \exp\left[ -\frac{(E_{\text{tr}} - E)}{kT} \right] \), \( x = r \cos(\theta) \), \( \theta = 0 \) (the right side), and \( \theta = \pi \) (the left side). Vertical and horizontal strokes respond to thermally activated and non-activated hopping, respectively.

\[ U_* = 2\gamma r + \frac{E' - eFr \cos(\theta) - E}{kT} \equiv \frac{E_{\text{tr}} - E}{kT}, \quad (1) \]
where $\gamma$ is inverse localization radius, $e$ – elementary charge, $T$ – absolute temperature, $k$ – Boltzmann constant, and $r_c$ is the maximum distance of hopping to a state of the energy $E'$. Eq. Источник ссылки не найден. yields the value of $r_c(F, E', \theta)$,

$$r_c(F, E', \theta) = \frac{(E_e - E')/(2\gamma kT - eF \cos \theta)}{(2)}$$

Eqs. Ошибка! Источник ссылки не найден. are valid under the condition $E' - eFr_i \cos \theta - E > 0$, hence $r_c < r_m \equiv (E' - E)/eF \cos \theta$. Otherwise, one has thermally non-activated jumps, hence $U* = 2\gamma r_0$. Obviously, $r* < r_0$, $r_m < r_0$.

The area in $E$-$r$ space, which is defined by the condition $\cos \theta = 0$, is shown in the Fig. 1, providing that the field is weak enough, $F < F_0 = 2\gamma kT/e$. In this case, $2\gamma kT > eF$, hence $E_o > E'$ at any hopping direction, i.e. at any angle $\theta$. Otherwise, if $F > F_o$, a physical condition $r_c > 0$ requires $E' > E_o$, providing that $\cos \theta > F/F_o$, see Eq. Источник ссылки не найден.. A carrier performs thermally activated jump over a distance $r \leq r_*$, if $E_{max} \geq E' \geq E_m(x) = E + eFx$, $x = r \cos \theta$, see Fig. 1, and one can find a value of $E_{tr}$ from the following equation:

$$B = 2\pi N_t \int_{-\infty}^{E_0} d\theta \sin \theta \int_{-\infty}^{E_{max}(E_0, r, 0)} dE' g(E'),$$

where $r_0 = U_0/2\gamma = (E_o - E)/2\gamma kT$, $N_t$ is the spatial concentration of localized states, randomly distributed in space. The value of $B$ (percolation factor) exceeds unity, because a fastest jump, which corresponds to $B = 1$, is typically followed by return to initial state according to Nikitenko and Strikhanov (2014), Baranovskii et al. (2002). One can express integrals in the right-hand side of Eq. (3) in terms of error functions, but the resulting expression is rather ponderous, hence it is not presented here. Worth noting, the value of $E_{tr}$ can be considered as a formal transport level, i.e. as a formal analogy of "mobility edge", if it does not depend on initial energy, $E$, but the result of Eq. (3) depends on $E$, in general. One can expect, however, according to Bässler et al. (1995), that the value of $E_{tr}$ is $E$-independent in a broad region of $E$, if energetically upward hopping dominates. Indeed, an analysis of Eq. (3) yields the following $E$-independent equation in the case of rather weak field and $E \to -\infty$,

$$B = \frac{2\pi N_t}{3} \int_{-\infty}^{E_0} dE' g(E') \int_{-\infty}^{\infty} d\theta \sin \theta r^3(E', \theta), \ F \ll F_o.$$ (4)

The same equation has been employed by Nikitenko and Strikhanov (2014), but now the distance, $r_c$, depends on the angle $\theta$ and on the field strength, see Eq. Источник ссылки не найден.. Integration in Eq. (4) yields:

$$B_{eff}(f) = \frac{\sqrt{2\pi N_t}}{6} \left( \frac{\sigma}{\gamma kT} \right)^3 \left[ \exp(-e_{tr}^2)(1 + e_{tr}^2) + e_{tr}(3/2 + e_{tr}^2)\operatorname{erfc}(-e_{tr}) \right],$$ (5)

where $B_{eff} = B(1 - f^2)$, $e_{tr} = E_{tr}/\sqrt{2\sigma}$, $f = F/F_o = eF/2\gamma kT$, and $\operatorname{erfc}(x)$ is the complementary error function. In the opposite limiting case of strong field, $F \gg F_o$, thermally non-activated hopping in the direction of electric force dominates the transport. In this limit, one can assume $E_{tr} - E = \text{const}$, according to Bässler et al. (1995). Estimating integrals in Eq. (3), one obtains

$$E_{tr} = 2\gamma a_{tr} kT + E, \ a_{tr} = \left(3B/2\pi N_t\right)^{1/3}, \ F \gg F_o.$$ (6)

Precise, see Eq. (3), and approximated, see Eqs.
(5), dependences \( E_{\nu} (E) \) are compared at various field strengths in the Fig. 2. One can conclude, that an energy-independent transport level from Eq. (5) is a good approximation, at least up to energies \( -\sigma^2/kT \), at typical values of disorder parameters, \( \sigma/kT \geq 2 \), if \( F/F_e \leq 0.5 \). Otherwise, it seems that the model of effective transport level violates. However, Eq. (6) shows, that the expression of typical hopping rate, \( \nu = v_0 \exp (-E_{\nu}/kT) \), yields physically reasonable asymptotic for non-activated hopping, \( F/F_e >> 1 ; \nu = v_0 \exp (-2\gamma a_0) \), being field-independent (saturation of drift velocity), see the work by Bässler et al. (1995). This circumstance encourages challenging an applicability of the effective transport level concept for the modeling of charge mobility in a broad area of field strengths.

![Fig. 2. Dependences of \( E_{\nu} \) on initial energy \( E \), parametric in dimensionless field strength, \( f = F/F_e \), as is shown in a figure. Solid and dashed lines are calculated from Eqs. (4) and (6), respectively, dash-dotted line – from Eq. (6), \( B = 2.8, 2\gamma N_i^{-1/3} = 10 \).](image)

Operationally, one can extend a multiple trapping (MT) model, considering \( E_{\nu} \) as an energy-dependent “mobility edge” and obtain the following expression of mobility, like Nikitenko and Strikhanov (2014) did:

\[
\mu \approx \mu_0 a^2 \int_{-\infty}^{\infty} \left( \frac{E_{\nu}}{kT} - E \right) \exp \left( \frac{E_{\nu} - E_{\nu}(f)}{kT} \right) d\varepsilon,
\]

where \( \mu_0 = e\nu_0 a_0^2 / (6\sigma) \), \( a = (E_{\nu} - E_{\nu}(f)) / (2\gamma a_0 kT) \approx 1 \) is a dimensionless typical hopping distance. Because of variable-range hopping, this value differs from the mean inter-site distance, \( a_0 = N_i^{-1/3} \). Eq. (7) means that all states are considered as “traps”, which is approved by convergence of the integral in the region of negative energies, if field is not very strong. If \( f \leq 0.5 \), one can consider \( E_{\nu} \) as field-independent, see Fig. 2, and Eq. (7) reduces to the well-known form, see Nikitenko and Strikhanov (2014), Bässler et al. (2007), Baranovskii et al. (2000), Baranovskii et al. (2002), Arkhipov et al. (2001):

\[
\mu \approx \mu_0 a^2 \exp \left( -\frac{1}{2} \left( \frac{\sigma}{kT} \right)^2 - \frac{E_{\nu}(f)}{kT} \right),
\]

where \( E_{\nu}(f) \) is determined from Eq. (5). The real (physical) transport level \( E_{\nu}(f) \) is calculated according to Nikitenko and Strikhanov (2014), replacing \( B \) by \( B_{\text{eff}}(f) \), see Eq. (6), if \( f \leq 0.5 \), and \( E_{\nu}(f) = E_{\nu}(0.5) \), if \( f > 0.5 \).

Fig. 3 shows field dependences of the mobility at different temperatures, as is calculated by different ways and is compared with results of Monte-Carlo simulations by Bässler (1993) (filled symbols). In the low-field limit, \( B_{\text{eff}}(f) \)
\[ B_0 = 2.2 + 0.2(\sigma / kT - 1.5), \quad \sqrt{2} \leq \sigma / kT \leq 4, \]
which provides precise temperature dependence of zero-field mobility corresponding to Nikitenko and Strikhanov (2014). \( N_r = 4.63 \times 10^{27} \text{m}^{-3}, \) as in the work by Bäßler (1993). Fig. 3 shows results of two analytic approaches, based on Eqs. (5) and 
\[ (8). \quad \text{In the first case, } B_{\text{eff}}(f) = B_0(1 - f^2)^2 \text{ in Eq. (5), as it results from Eq. (4) (dashed line), while in the second case } \]
\[ B_{\text{eff}}(f) = B_0(1 - f^2)^2 = B_0(1 - f^2)^2 \text{ is applied (solid line), in order to achieve a better agreement with } \]
Monte-Carlo results of mobility. One needs to modify \( B_{\text{eff}}(f), \) introducing operationally the field-dependent percolation factor \( B(1 - f^2)^2 \) in Eq. (5), because 1) not a single level \(-\sigma^2/kT\), but a relatively broad interval of initial energies around and above this level contributes to mobility, and 2) energy dependence of \( E_{tr} \) becomes considerable within this interval at \( f \approx 0.5 \), see Fig. 2. An effective value of \( E_{tr} \), which is necessary to fit MC-result of mobility at \( f = 0.5 \), and respective effective initial energy are the ordinate and the abscissa of the point in the Fig. 2.

Fig. 3. Field and temperature dependences of the mobility. Solid and dashed lines are calculated from Eqs. (5), (8) with effective percolation factor \( B_{\text{eff}} = B(1 - f^2)^2 \) and \( B_{\text{eff}} = B_0(1 - f^2)^2 \), respectively, lines with circles (red online) – result of Eqs. (3), (7). Filled symbols – Monte Carlo simulation by Baranovskii et al. (2002) at \( \sigma / kT = 2 \) (squares), 2.5 (circles), 3 (up triangles) and 3.5 (down triangles). Arrow marks the value of \( F = 0.5F_c \) at \( \sigma / kT = 3.5 \).

One has to note that the value of \( f = 0.5 \) responds to rather high field strength, \( 1.4 \times 10^6 \text{ V/cm, at } \sigma / kT = 3.5. \) Fig. 3 shows that the analytic model with modified (field-dependent) value of \( B \) (solid lines) and MC simulations are in good agreement at \( f \leq 0.5. \) Moreover, extended version of transport level concept, see Eq., (7), yields surprisingly good description of field dependence of mobility at stronger fields, if disorder is considerable (lines with open circles), although the analogy with multiple trapping is violated at strong field, \( f \approx 1. \) Non-modified (field-independent) percolation factor \( B = B_0 \) has been used in calculations with Eqs., (3), (7), confirming that an apparent field dependence of \( B \) originates from energy dependence of formal transport level, \( E_{tr}. \)

In conclusion, some remarks about an effect of concentration of charge carriers on transport level. Previously, this effect was analyzed by Baranovskii et al. (2010) via account of filling of final states, i.e. replacing \( g(E') \) in Eq. (3) by the density of free states, \( g(E')(1 - f(E')) \), where \( f(E') \) is Fermi function. As a result, transport level shifted towards high energies. We add an effect of Coulomb interaction of neighbor charges. On a qualitative level, we assume that a concentration is rather small in order to account for only nearest neighbor, providing that the distance is equal to the average intercharge distance, \( r_i = (3 / (4\pi c N_r))^{1/3}, \) where \( c \) is relative concentration of carriers. The Coulomb field around the initial state is nearly uniform, \( F = e / (4\pi \varepsilon_0 \varepsilon r_i^2), \) and we can use a formalism, described above, in order to calculate transport level. Fig. 4 shows concentration dependence of transport energy at \( \sigma = 3.5kT \) in three cases. In the first case Coulomb...
interactions are neglected but filling of localized states is taken into account. Second approach considers only filling of localized states. Both Coulomb interactions and filling of localized states are taken into account in third case.

Fig. 4 illustrates, that Coulomb interaction yields to opposite effect, than filling of states. One needs in more accurate analysis in order to quantify both effects.

![Fig. 4. Concentration dependence of transport energy at different approaches. Solid line is approach where Coulomb interactions are neglected, \( F = 0 \); dash line is approach where filling states is taken into account; dot line is approach where Coulomb interactions and filling states are taken into account.](image)

3. Results

In summary, the main result of this work is an extension of effective transport level concept by Nikitenko and Strikhanov (2014) and demonstration of its applicability to modeling of mobility at rather strong field, at least \( F \leq \gamma kT/e \), i.e. up to strength of the order of \( 10^6 \) \( V/cm \) at typical values of parameters, that is enough for numerous applications in organic electronics. This result is obtained in the framework of Gaussian disorder model, while the field dependence of mobility describes better by correlated disorder model by Novikov et al. (1998). However, a transport level concept of effective transport level in weak-field limit seems to be applicable under the presence of energetic correlations, too, according to recent works by Cotaar et al. (2012), Nikitenko et al. (2014). Analytic description of field dependence of mobility by means of effective transport level in the case of energetic correlations is a subject of future work.

Acknowledgements

This work was supported by Ministry of Education and Science of Russian Federation, Agreement No. 14.575.21.0002, ID RFMEFI57514X0002.

References