Validity of Transport Energy in Disordered Organic Semiconductors

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A systematic study of the transport energy in disordered organic semiconductors based on variable range hopping theory has been presented here. The temperature, electric field, material disorder and carrier concentration dependent transport energy is extensively discussed. We demonstrate here, transport energy is not a general concept and invalid even in low electric field and concentration regime.

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Understanding the charge transport mechanism in disordered organic semiconductors such as conjugated and molecularly doped polymers, is of crucial importance to design and synthesize better materials. Physical transport phenomena in organic semiconductors are in general very complex and arise from energy and spatial disorder, which invalidates the use of the traditional band transport theories based on the periodic distribution of atoms in inorganic crystals. Currently, charge transport in organic semiconductors is often described in terms of hopping theory [1]. A fundamental work in the modeling of the hopping transport in organic semiconductors is the Gaussian disorder model proposed by Bassler [2, 3]. Subsequent to this Monte Carlo simulation, a number of theoretical investigations concerning charge transport in amorphous organic systems utilizing the Gaussian approach have been published and considerable progress in the analytical description of the problem has been made [4–7]. An important simplification of the complex hopping transport mechanism was the introduction of the concept of transport energy. This concept allows the complex hopping mechanism in the band tails to be interpreted in terms of a multiple-trapping-and-release model, where the transport energy plays the role in the mobility edge in amorphous inorganic semiconductors [8–13]. Thermally stimulated luminescence [14], carrier dependent mobility [10, 15, 17], seebeck coefficient [18], as well as injection phenomena [19], have already been described utilizing this transport energy concept. Despite the concept of transport energy has widely been applied in organic semiconductors, both of them are based on the Miller-Abrahams expressions [20], the hopping transport takes place via tunneling between an initial states and a target states. The tunneling process is described as

\[ \nu = \nu_0 \exp (-u) = \nu_0 \left\{ \begin{array}{ll} \exp \left( -2\alpha R_{ij} - \frac{E_j - E_i}{kT} \right), & E_i > E_j \\ (-2\alpha R_{ij}), & E_i < E_j \end{array} \right. \]

Here, \( \nu_0 \) is the attempt-to-jump frequency, \( R_{ij} \) is the hopping distance, \( u \) is the hopping range, \( E_i \) and \( E_j \) are the energies at site \( i \) and \( j \), respectively, \( \alpha \) is the inverse localized length and \( k \) is the Boltzmann constant. Then, if only the hopping upwards \( \nu_\uparrow \) is taken into account, the transport energy is defined as the final energy \( E_i \) that the hopping transport has maximum rate, so \( E_i \) could be obtained by the equation as [12]

\[ \frac{\partial \nu_\uparrow}{\partial E_i} = 0. \]

This gives

\[ g(E_i) \left[ \int_{-\infty}^{E_i} g(E) \, dE \right]^{-4/3} = \frac{1}{\alpha kT} \left( \frac{9\pi}{2} \right)^{1/3}. \]

Where \( g(E) \) is the density of states (DOS). Here we can see that the hopping transport is limited by upward transitions from filled states to empty states and the transport energy has been derived as the preferred energy to which the fastest upward transitions occur.

In the other case, the transport energy is derived based on the average number of target sites \( n(E_i, u) \) as

\[ n(E_i, u) = \int_0^{u_2} R_{ij}^2 dR_{ij} \int_{-\infty}^{E_i + kT(u-2\alpha)} g(E) \, dE. \]
If we disregard the hopping downwards and choose the starting energy $E_i$, as $-\infty$, the transport energy could be obtained by setting $n(E_i, u) = 1$ and the result is 

$$\int_{-\infty}^{E_i} g(E)(E_i - E)^{\frac{3}{2}} dE = \frac{6}{\pi} (\alpha kT)^{\frac{3}{2}}.$$  

(5)

This definition hints that the transport energy is the site energy to which the hopping upwards need the least energy in energy space. When there exists an electric field $F$, the electric field will lower the Coulomb barrier, which leads to the reduction of the thermal activation energies, and the hopping range with normalized energy can therefore be rewritten as 

$$u = \begin{cases} 2\alpha (1 + \beta)R_{ij} + \epsilon_j - \epsilon_i, \epsilon_j > \epsilon_i - \beta \cos \theta \\ (2\alpha R_{ij}) \end{cases}$$  

(6)

Where $\beta = F\epsilon/2\alpha kT$ and $\theta$ is the angle between $R_{ij}$ and the electric field ranging from 0 to $\pi$. For a site with energy $\epsilon_i$ in the hopping space, the most probable hop for a carrier on this site is to an empty site at a range $u$, where it needs the minimum energy. Conduction is the result of a long sequence of hops through this hopping space. Then, following the method in [21], we derive the number of empty sites enclosed by the constant range $u$, as 

$$n(\epsilon_i, F, u) = \frac{1}{8\alpha^3} \int_{0}^{\pi} d\theta \sin \theta \int_{0}^{u} dr 2\pi r^2 \int_{-\infty}^{u + \epsilon + r(1 + \beta \cos \theta)} d\epsilon \times g(\epsilon) [1 - f(\epsilon, \epsilon_F)]$$  

(7)

Here $f(\epsilon, \epsilon_F)$ is the Fermi Dirac distribution and $1 - f(\epsilon, \epsilon_F)$ is the probability that the final site is empty, the Fermi energy $\epsilon_F$ is calculated by the condition 

$$c = \int_{-\infty}^{\epsilon_F} d\epsilon \frac{g(\epsilon)}{1 + \exp(\epsilon + \epsilon_F)}.$$  

(8)

Here $c$ is the carrier concentration. By change the integration variable, equation (7) will be in the form of 

$$n(\epsilon, u, F) = \frac{2\pi}{3 \times 8\alpha^3} \int_{-1}^{1} d\tau \times \left[ \int_{\epsilon_i^{-} - \beta u\tau}^{\epsilon_i^{+} + u} d\epsilon g(\epsilon) \frac{(u + \epsilon_i - \epsilon)^3}{(1 + \beta\tau)^2} + \int_{-\infty}^{\epsilon_i^{-} - \beta u\tau} d\epsilon g(\epsilon) \right]$$  

(9)

The first term on the right-hand side of equation (9) gives the number of shallower states, and the second one describes the number of target states which are deeper than the starting site. According to the variable range hopping theory [6, 16, 21], at a given field and temperature, almost every starting localized state has only one well distinguished nearest empty target hopping neighbor, i.e., another localized state that is characterized by the minimum value of the hopping range, this range could be obtained by solving the equation 

$$n(\epsilon_i, F, u) = 1.$$  

(10)

This equation established the basis of our model. The target site energy for every hopping process can be well evaluated from the equation (10).

**Validity of Arkhipov transport energy.**—To check this model validity, we disregard the downwards hopping as well, equation (9) then reads as 

$$1 = \frac{2\pi}{3 \times 8\alpha^3} \int_{-1}^{1} d\tau \int_{\epsilon_i^{-} - \beta u\tau}^{\epsilon_i^{+} + u} d\epsilon g(\epsilon) \frac{(u + \epsilon_i - \epsilon)^3}{(1 + \beta\tau)^2}$$  

(11)

Using the developed model equation (11), we now proceed to calculate the relation between starting energy and final energy in real disordered organic semiconductors. We take the Gaussian form $g(\epsilon) = \frac{N_i}{\sqrt{\pi} \sigma} \exp\left(-\frac{\epsilon^2}{2\sigma^2}\right)$ density of states in the full manuscript, where $N_i$ is the number of states per unit volume and $\sigma = \sigma_0/kT$ indicates the width of the DOS. $N_i = 1 \times 10^{29}m^{-3}$ is taken in the full manuscript, a typical value for the relevant organic semiconductors. It is instructive to calculate this target energy as a function of the initial energy for different carrier concentration, corresponding to different fermi-level, the results are displayed in the insert of Fig. 1. A clear observation is that, in this situation, the transport energy does exist for deeper starting energy but increases with the carrier concentration. Field dependent transport energy is plotted in the Fig.1, the same as concentration dependent transport energy, field does not change transport energy for deeper energies but decreases for field higher than $1 \times 10^5V/m$, this field strength is actually low field for most organic devices. The reason for the decrease of transport energy is that, the electric field can change the energy difference between the final and target sites, and thereby, assist carrier jumps along the field direction, so the target energy will decrease on the contrary. For the very low carrier concentration, the field and concentration dependent transport energy could be derived as 

$$n(\epsilon, u, F) \approx \frac{2\pi}{24\alpha^3 (1 - \beta)^2} \int_{\epsilon_i^{-} - \beta u\tau}^{\epsilon_i^{+} + u} g(\epsilon) (u + \epsilon_i - \epsilon)^3 d\epsilon$$  

$$= \frac{2\pi}{24\alpha^3 (1 - \beta)^2} \int_{-\infty}^{\epsilon_i^{-} - \beta u\tau} g(\epsilon) (u + \epsilon_i - \epsilon)^3 d\epsilon$$  

(12)

Certainly, this is not a general concept as well. We then consider the effect of the lattice disorder, which is caused by the random molecular packing in organic semiconductors [23]. The relation between transport energy and materials disorder $\sigma$ is shown in Fig. 2 (a). An important result is that, the transport energy is invalid for higher energies, but these energies make sense for the charge transport in real organic semiconductors.
It is well known, in the low carrier concentration regime, the hopping usually jumps from the so-called equilibrium energy $E_{\infty} = -(\sigma / kT)^2 = -25kT$ for $\sigma / kT = 5$; In the high carrier concentration regime, the carrier jumps from Fermi energy ($\epsilon_F = -20k_BT$ here). An obvious feature appears here is the transport energy does not exist for energy higher than $-18kT$ in the case of $\sigma / kT = 5$. In organic semiconductors, $\sigma = 5kT$ correspond to $\sigma = 0.12eV$ at room temperature, a typical value for organic semiconductors [24]. Therefore, the transport energy has no generality and is invalid for real organic semiconductor system. Please note that the field used here is $1 \times 10^5 V/m$, which is low field regime; the fermi energy chosen here is also corresponding to the low concentration regime. The other parameters values are also typical ones for organic semiconductors such as $\alpha = 1nm$. To investigate the reason for this phenomena, we plot the ratio between downwards and upwards hopping in Fig. 2(b), one can see clearly that, the downwards hopping has little effect on the charge transport characteristics and should not account for this result. One possible explanation is, for the small disorder Gaussian DOS, since the carriers have few nearest neighbor sites to choose and it is reasonable to hop to the same energy; But for the wider Gaussian DOS, carriers has more near neighbor sites and more active, hence the target energy will be random according to the calculation. Therefore, the approximation in [6, 12] that the the transport energy in zero field is independent the starting energy is not correct in real organic semiconductors.

The question arises now on how much difference between the calculated mobility using Akhipov method and the work here. The comparison is shown in Fig. 3. It is clearly seen that, in the low temperature regime, Akhipov model will underestimate the mobility but overestimate the mobility in high temperature. And this trend is even more pronounced with carrier concentration increasing.

Validity of Baranovskii transport energy model.—

According to the definition of Baranovskii transport energy, the hopping upwards rate has maximum value for every jumping, hence, we derive equation (6) as

$$
\frac{\partial \nu_i}{\partial \epsilon_j} = 2\alpha (1 + \beta) \frac{\partial R_{ij}}{\partial \epsilon_j} + 1 = 0,
$$

$$
\frac{\partial \nu_i}{\partial \epsilon_j} = 2\alpha (1 + \beta) \frac{\partial R_{ij}}{\partial \epsilon_j} = 0,
$$

$$
1 = 4\pi R_{ij}^2 \int_0^\theta \sin \theta d\theta \int_{-\infty}^{\epsilon_j} d\epsilon \left[ 1 - f(\epsilon, \epsilon_F) \right].
$$

(13)

The $R_{ij}$ that is the function of $\theta$ and $\epsilon_j$, could be obtained as the equation (11). Connecting Gaussian DOS and equation(12), we numerically calculate the transport energy for this definition. The concentration dependent transport energy is shown in Fig. 4. The deviation of target energy from the transport energy is more dramatic, even at the starting energy $\epsilon_i = 24k_BT$, the transport energy is obvious invalid. This holds for the field dependent transport energy (the insert figure), too. We also find, the same conclusion is obtained by introducing the percolation parameter 12 in equation (13).

In conclusion, the validity of the transport energy in disordered organic semiconductors has been investigated intensively. The results shows, neither Baranovskii nor...
Arkhipov definition for the transport energy is valid in real organic semiconductors system, even in the low field regime, the transport energy lost the universality. This issue was not adequately addressed for in earlier evaluations of the transport energy based on the hopping rates. Concomitantly, the use of the previously obtained expressions for transport energy in calculations of the carrier transport parameters would lead to incorrect results for the concentration dependencies of these parameters [18, 22, 24]. It should be mentioned that these calculations are describing only the first release step. These oscillating jumps of the released carriers may jump back to their initial state do not contribute effectively to the charge transport [9]. Finally, we mention that the description presented here should also be applicable to describe the temperature, electric field and carrier concentration dependent charge transport properties, for example mobility, as we have done in [22].

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[1] N. F. Mott, J. Phys. C 20, 3075 (1987).
[2] H. Bassler, Phys. Status Solidi B Res. A 175, 15 (1993).
[3] H. Bassler, Phys. Status Solidi B Res. A 107, 9 (1981).
[4] S. N. Novikov, D. H. Dunlap, V. M. Kenkre, P. E. Parris, and A. V. Vannikov, Rev. Lett. A 81, 4472 (1998).
[5] D. H. Dunlap, V. M. Kenkre, P. E. Parris, and A. V. Vannikov, Rev. Lett. A 77, 542 (1996).
[6] V. I. Arkhipov, E. V. Emelianova, and H. Bassler, Philos. Mag. B 81, 985 (2001).
[7] L. Li, G. Meller, and H. Kosina, Appl. Phys. Letter. 98, 023305 (2011).
[8] D. Monro, Phys. Rev. Lett. 54, 146 (1985).
[9] V. I. Arkhipov, E. V. Emelianova, and G. J. Adriaenssens, Phys. Rev. B 64, 985 (2001), 125125(2001).
[10] L. Li, G. Meller, and H. Kosina, Appl. Phys. Lett. 92, 013307 (2008).
[11] S. D. Baranovskii, H. Cordes, S. Yamasaki, and P. Thomas, Phys. Status Solidi B 230, 281 (2002).
[12] O. Rubel, S. D. Baranovskii, H. Cordes, P. Thomas, and S. Yamasaki, Phys. Rev. B 69, 014206 (2004).
[13] R. Schmehel, J. Appl. Phys. 93, 4653 (2003).
[14] A. Kadashchuk, Y. Skryshevskii, A. Vakhnin, N. Ostapenko, V. I. Arkhipov, E. V. Emelianova, and H. Bassler, Phys. Rev. B 63, 115205 (2001).
[15] C. Tanase, E. G Meijer, P. W. M. Blom, and D. M. de Leeuw, Phys. Rev. Lett 91, 216601 (2003).
[16] J. O. Oelerich, D. Huemmer, and S D. Baranovskii, Phys. Rev. Lett. 108, 226403 (2012).
[17] M. C. J. M Vissenberg, and M. Matters, Phys. Rev. B 57, 12964 (1998).
[18] W. Chr. Germs, K. Guo, R. A. J. Janssen, and M. Kemering, Phys. Rev. Lett. 109, 016601 (2012).
[19] V. I. Arkhipov, U. Wolf, and H. Bassler, Philos. Mag. B 59, 7514 (1999).
[20] A. Miller, and E. Abraham, Phys. Rev. B 120, 745 (1960).
[21] N. Apsley, and H. P. Hughes, Philos. Mag. 31, 1327 (1975).
[22] L. Li, S. Winkel, J. Genoe, and P. Heremans, Appl. Phys. Lett. 95, 153301 (2009).
[23] I N. Hulea, H. B. Brom, A. J. Houtepen, D. Vannakelbergh, J. J. Kelly, and E. A. Meuenkamp, Phys. Rev. Lett. 93, 166601 (2004).
[24] W. F. Pasveer, J. Cottaar, C. Tamase, R. Coehoorn, P. A. Bobbert, P. W. M. Blom, D. M. de Leeuw, and M. A. J. Michels, Phys. Rev. Lett. 94, 206601 (2005).
[25] L. Li, G. Meller, and H. Kosina, J. Appl. Phys. 106, 013714 (2008).
[26] V. I. Arkhipov, E. V. Emelianova, G. J. Adriaenssens, and H. Bassler, J. Non-Crys. Solids 299, 1047 (2002).
[27] R. Coehoorn, W. F. Pasveer, P. A. Bobbert, and M. A. J. Michels, Phys. Rev. B 72, 155206 (2005).