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Exponential-type density of states with clearly cutting tail for organic semiconductors

Xiao-Hong Shi [a], Jiu-Xun Sun [a, b, *], Chun-Hua Xiong [a], Le Sun [a]

[a] School of Physical Electronics, University of Electronic Science and Technology, Chengdu 610054, China
[b] Laboratory for Shock Wave and Detonation Physics Research, Southwest Institute of Fluid Physics, Mianyang 621900, China

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ABSTRACT

It was recently demonstrated that the density of states (DOS) is the key factor to determine charge transport, photoelectric and contact properties in disordered organic semiconductors. However, the density of states in organic semiconductors is unclear at present. Although the Gaussian DOS is the most popular, some works support the exponential DOS or combination of both forms. In this paper, we propose three exponential-type DOS, one has complete exponential tail, and other two cuts tails at some places. The variations of mobility with carrier density are obtained through numerically solving variable range hopping (VRH) equations. It is shown that the relationships of mobility with density and Fermi level are very different among results obtained from Gaussian, un-cutting and cutting exponential-type DOS. The results show that the experimental mobility-density data can be well fitted by using single cutting exponential-type DOS in the wide ranges of density, but cannot be fitted by using single Gaussian and un-cutting exponential-type DOS. Instead of the Gaussian and pure exponential DOS, the DOS with exponential core and clearly cutting tail is recommended.

1. Introduction

Organic electronics is emerging as a high potential technology for low-cost/large-area electronics. Disordered organic semiconductors are widely used in organic devices such as organic light-emitting diodes [1–3], field-effect transistors [4–7], and photovoltaic devices [8–12], and sensors [13,14]. However, the charge transport mechanism in organic semiconductors is unclear at present and the density of states (DOS) is the key factor to determine the charge transport and photoelectric properties of these materials [15–20]. Reliable first-principles calculations of the DOS in disordered organic materials are not accessible at present. The only way to determine the DOS is to compare experimental data with the appropriate theory using some trial DOS functions $D(E)$ to fit theoretical results with experimental data [15–20].

The Gaussian DOS (GSS) is the most popular in researches of organic semiconductors

$$D(E) = \left(N_0 \Big/ \sigma\sqrt{2\pi}\right)\exp\left[-(E-E_v)^2 \Big/ 2\sigma^2\right] \quad (1)$$

σ is the width, N_0 is the total concentration of states at energy levels E_v. The exponential DOS is also widely used for analytic formulae being accessible in some models

$$D(E) = (N_0/\sigma)\exp[(E-E_v)/\sigma], \quad (-\infty < E \le E_v) \quad (2)$$

Considering that the results for the p- or n-type case are exactly symmetric, we merely give the expressions and results for p-type semiconductors for clarity unless otherwise specified. Bässler [15] firstly proposed the Gaussian disorder model (GDM). The disorder is modeled by a Gaussian distribution of on-site energies. Pasveer et al. [16] extended the GDM and constructed a parameterization of the mobility function based on a numerically solution of the master equation and the Miller-Abrahams (MA) hopping rates. Cottaar et al. [17] developed a scaling theory through extending percolation theory. A general expression of mobility is given for MA and Marcus hopping rates with Gaussian energy disorder and without application to real materials. Fishchuk et al. [18,19] also proposed the effective medium approximation theory as an extension of GDM.

Vissenberg and Matters (VM) [20] derived an analytic

* Corresponding author. School of Physical Electronics, University of Electronic Science and Technology, Chengdu 610054, China.
E-mail address: sjx@uestc.edu.cn (J.-X. Sun).

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expression of mobility based on the exponential DOS in Eq. (2) through analytically solving the variable range hopping (VRH) equations from the percolation model. However, the analytic expression cannot be extended to other DOS, Torricelli et al. [21] numerically solving the VRH equations for the Gaussian and mixing DOS. By comparing numerical results of mobility with experimental data, they [21] concluded that a single Gaussian DOS is incapable to explain the mobility behavior in the whole range of concentrations. Depending on the material, it could be accurately approximated by a single Gaussian, an exponential, or by a combination of both functions. The DOS they proposed is given by Eq. (3)

$$D_T(E) = \min\left\{ N_0^E \exp\left(\frac{E-E_v}{k_B T_0^E}\right)\Theta(E_v - E), \left(\frac{N_0^G}{\sigma_G\sqrt{2\pi}}\right) \exp\left[-\frac{(E-E_v)^2}{2\sigma_G^2}\right]\right\} \tag{3}$$

where N_0^E, T_0^E, N_0^G,σ_G and E_v are five parameters.

Some authors [22,23] derived approximate expression based on the percolation model and some new concepts, such as mean energy of hopping carriers, median rates of downward and upward hops, average hopping time etc. Oelerich et al. [23] proposed following general DOS with λ as the adjustable parameter

$$D(E) = (N_0/\sigma)\exp\left[-(E_v - E)^{\lambda}\Big/\sigma^{\lambda}\right], \quad (-\infty < E \le E_v) \tag{4}$$

through qualitatively comparing their expression with experimental data. They [23] concluded that λ should take values larger than 1.8, and the model is more close to the Gaussian form. Welborn et al. [24] used free probability to approximate the DOS in tight-binding models of disordered electronic systems; they found that the DOS can take both Gaussian and non-Gaussian forms for different parameter values.

Kirchartz et al. [9] researched recombination mechanism of organic solar cells, they pointed out that in order to correctly reproduce this experimental data, it is necessary to include an exponential tail of DOS for both electrons and holes and allow recombination to occur between free charge carriers and charge carriers trapped in these states. Hawks et al. [25] analytically studied recombination through band tail localized states. By comparing with measurement for three different organic solar cells, they confirmed [25] that the band tail recombination mechanism applies to at least some organic solar cells.

Lange et al. [26] observed significant band bending in four different conjugated polymers when deposited on a substrate with a high or low work function, and proposed a model to explain band bending successfully. Since the models based on both Gaussian and exponential DOS could well describe experimental data, they [26] failed to judge which DOS is favorite. Oehzelt et al. [27] extended band bending model of Lange et al. [26] and established general electrostatic model basing on Gaussian DOS. Their results [27] highlighted that the DOS in organic semiconductor is a key factor. It can determine the minimum value of practically achievable injection barriers as well as their spatial profile. Bubnova [28] measured and analyzed the thermoelectric properties of various poly(3,4-ethylenedioxythiophene) samples. Their results show that the Seebeck coefficient is strongly depended to DOS and proportional to $[\mathrm{d}(\ln N(E))/\mathrm{d}E]_{E=E_F}$. Mendels and Tessler [29] investigated the thermoelectric properties of disordered organic semiconductors under the premise of the GDM and its variants by using Monte Carlo simulations. Their results shown that the GDM can qualitatively describe thermoelectricity in organic semiconductors.

From above statement, it is clear that the DOS is a key factor in organic semiconductors [15–29]. It determines transport properties [15–24], and photoelectric properties [9,25,28,29], as well as interface properties of organic semiconductors with electrode materials [26,27]. However, the shape of DOS is still a controversial issue. Most literature supported the Gaussian DOS [15–19,22,23,26–29]; some preferred the exponential shape [9,20,21,25,26]; few encouraged combination of Gaussian and exponential shape [21]. In this paper, by comparing numerical solutions of VRH equations with experimental data of mobility in literature, we propose several exponential-type DOS. It is shown that the results from exponential-type DOS with clearly cutting tail can well fit the experimental data in the whole range of concentrations.

2. Model theory and three exponential-type DOS

The charge carriers in disordered organic materials have been recognized as highly localized [15–30]. Charge-carrier transport is determined by hopping between different sites. The Miller-Abraham (MA) rate is usually used to describe hopping of a carrier between two localized sites i and j [15–23]:

$$w_{ij} = \begin{cases} \nu_0 \exp\left[-2\alpha r_{ij} - \beta(E_j - E_i)\right], E_j \ge E_i \\ \nu_0 \exp\left[-2\alpha r_{ij}\right], E_j < E_i \end{cases} \tag{5}$$

where w_{ij} is the hopping transition rate, α^{-1} is the localization radius of a charge carrier, r_{ij} is the distance between sites i and j, $\beta = 1/k_B T$ is the temperature factor, and ν_0 is the attempt-to-escape frequency.

The system can be regarded as a random resistor network as proposed by Miller-Abram [19,22–24]. In this case, the conductance between the sites i and j can be described as $G_{ij} = G_0 e^{(-s_{ij})}$ where s_{ij} is:

$$s_{ij} = 2\alpha r_{ij} + 0.5\beta(|E_i - E_F| + |E_j - E_F| + |E_i - E_j|) \tag{6}$$

E_F is the Fermi energy level of the material. According to the percolation theory, the conductivity G of the system can be written as

$$G = G_0 \exp(-s_c) \tag{7}$$

where G_0 is an unknown prefactor. s_c is the exponent of the critical percolation conductance, it can be solved from following equation

$$B_c = \frac{N_b(s_c, E_F)}{N_s(s_c, E_F)} \tag{8}$$

In the percolation system N_b is the density of bonds, N_s is the density of sites. B_c is the critical average number of bonds per site, for a three-dimensional amorphous system B_c is equal to 2.8 [20]. The density of bonds N_b is given by:

$$N_b = 2\pi \int_{-1}^{1} dx \int_{R^+} r_{ij}^2 dr_{ij} \int_{R^2} \Theta(s_c - s_{ij}) D(E_i) D(E_j) dE_i dE_j \tag{9}$$

the density of sites N_s can be expressed as

$$N_s = \int_R D(E)\Theta(s_c - \beta|E - E_F|)dE \tag{10}$$

where $D(E)$ is the density of states, Θ is the step function that represents the percolation criterion. E_F is Fermi energy.