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Spin diffusion in disordered organic semiconductors

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An analytical theory for spin diffusion in disordered organic semiconductors is derived. It is based on percolation theory and variable range hopping in a disordered energy landscape with a Gaussian density of states. It describes universally the dependence of the spin diffusion on temperature, carrier density, material disorder, magnetic field, and electric field at the arbitrary magnitude of the Hubbard energy of charge pairs. It is found that, compared to the spin transport carried by carriers hopping, the spin exchange will hinder the spin diffusion process at low carrier density, even under the condition of a weak electric field. Importantly, under the influence of a bias voltage, anomalous spreading of the spin packet will lead to an abnormal temperature dependence of the spin diffusion coefficient and diffusion length. This explains the recent experimental data for spin diffusion length observed in Alq3.

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I. INTRODUCTION

Recently, considerable interests in spin transport in organic materials have been generated due to possible applications of organic spintronics [1–3]. Understanding spin transport is of crucial importance in designing and synthesizing better material and further improving device performances. One of the most important parameters describing the spin transport is the coefficient of spin diffusion. It is related to the Hanle effect in organic spin-valve structure. Although spin diffusion in organic semiconductors has been discussed in earlier work [4,5], neither the role of disorder of the material, the dependence of the charge carrier mobility on the concentration of charge carriers, nor the influence of an electric field has been explored. So, a unified theoretical description of spin diffusion is still lacking. Moreover, recent measurements conducted over a large range of temperature have established that in organic semiconductors, the spin diffusion length exhibits an unusual decrease with temperature [6]. Until now, no physical model could explain this behavior.

In this paper, we present a general analytical theory to describe the spin diffusion for organic semiconductors. It is based on percolation and hopping concepts and includes the spin exchange, bipolaron transport, and spin flip. The theory maps the complex phenomena of spin transport onto a simple problem of percolation contributed both by spin exchange and polaron hopping. This percolation based theory allows us to explain the measured temperature dependent spin diffusion length, as well as to make predictions of spin diffusion in high electric field and large carrier density. This approach is superior to an earlier analysis of spin diffusion by exchange coupling between localized states [4] because (1) it is universal in the sense that it incorporates the influence of temperature, electric field, magnetic field, disorder, charge carrier concentration, and the Hubbard energy of the polarons can be described, (2) it can identify the role of anomalous spreading of spin packet induced by electric field, and (3) it is based upon percolation theory to determine the spin diffusion coefficient in a disordered system rather than simply summing up the effects of spin exchange and polaron hopping [4]. We demonstrate that a decrease in the spin diffusion length with temperature arises naturally from the anomalous spreading of spin packet.

II. THEORY

Organic material films are usually a disordered system in which charge carriers (polarons) are localized. In polaron hopping, both charge and spin motion are coupled, and three processes should be considered simultaneously. The first process is polaron hopping toward an empty site, which carries both charge and spin currents. The second process is polaron hopping toward a singly occupied site, producing a doubly occupied state, i.e., bipolaron. For such double occupation, it is assumed that only singlets are allowed at a given site, with an energy penalty U, also called the Hubbard energy [5]. This process also carries both currents at the same time. The last process is the spin exchange coupling, which exchanges the spin state of two adjacent sites directly without phonon assistance [4]. This process results in a net spin current without charge motion. Considering these processes under quasiequilibrium condition, we start with the master equation for the conserved probability $P_i\uparrow$ that a particle is on site i with up spin

$$\begin{aligned}0 = &-\sum_j w_{i\to j} P_i\uparrow(1 - P_j\uparrow - P_j\downarrow)\\ &+\sum_j w_{j\to i} P_j\uparrow(1 - P_i\uparrow - P_i\downarrow)\\ &-\sum_j \tilde{w}_{i\to j} P_i\uparrow(pP_j\uparrow + P_j\downarrow)\\ &+\sum_j \tilde{w}_{j\to i} P_j\uparrow(pP_i\uparrow + P_j\downarrow)\\ &-\sum_j \eta_{i\to j} P_i\uparrow P_j\downarrow + \sum_j \eta_{j\to i} P_j\uparrow P_i\downarrow,\end{aligned} \quad (1a)$$

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$$w_{ij} = \begin{cases} v_0\exp\left(-2\alpha(1+\beta\cos\theta)R_{ij} - \frac{E_j-E_i}{k_BT}\right)\ E_j > E_i - 2\alpha\beta\cos\theta \\ v_0\exp(-2\alpha R_{ij})E_j < E_i - 2\alpha\beta\cos\theta \end{cases}, \tag{1b}$$

$$p = \frac{1}{3} - \frac{\int_0^\infty \exp(-t/\tau_h)\left(1 - \frac{{a_{\text{eff}}}^2t^2}{8}\left(1 + \frac{2\sin^2\omega_0t/2}{(\omega_0t/2)^2}\right)\right)dt}{3\tau_h}, \tag{1c}$$

where the first two terms correspond to conventional polaron hopping, the middle two to bipolaron formation, and the last two to spin exchange, respectively. In the above equation, $w_{i\to j}$ denotes the hopping rate from site i to an empty site j [7]; p is the probability of spin flip [8,9], $\eta_{i\to j} = 0.821\frac{q^2\alpha}{\varepsilon\hbar}(2\alpha R_{ij})^{5/2}\exp(-2\alpha R_{ij})$ denotes the probability for spin exchange [4]; v_0 is the attempt-to-jump frequency; α is the inverse localization radius; $\beta = qF/2\alpha k_BT$, with k_B being the Boltzmann constant, q being the elementary charge, and F being the electric field; ε is the dielectric constant; $\hbar$ is the Planck constant; R_{ij} is the distance between two sites; $\tau_h = {w_{ij}}^{-1}$ is the hopping time; the hyperfine precession frequency is $\omega_0 = \gamma_eB$, with B being the applied external magnetic field and γ_e being the gyromagnetic ratio; ${a_{\text{eff}}}^2$ is the effective hyperfine coupling width due to all the nuclei at a site; and t is the time. So far, we did not consider the effect of spin-orbit coupling. Based upon the work in Ref. [8], this effect could, however, be incorporated via changing the value of a_{eff}. $\tilde{w}_{i\to j}$ denotes the hopping rate from site i to a singly occupied site j with downward spin as

$$\tilde{w}_{ij} = \begin{cases} v_0\exp\left(-2\alpha(1+\beta\cos\theta)R_{ij} - \frac{E_j-E_i+U-\mathrm{V}}{k_BT}\right)\ E_j > E_i - 2\alpha\beta\cos\theta - U + V \\ v_0\exp(-2\alpha R_{ij})\ \ E_j < E_i - 2\alpha\beta\cos\theta - U + V \end{cases}. \tag{2}$$

Here U is the onsite Hubbard energy, which gives the energy cost of adding a second charge to a singly occupied site. Introducing finite U implies a nonzero probability of bipolaron formation, compared to a large U in conventional hopping models. An effective attractive interaction between polarons mediated by phonons can decrease U. In the case of strong interaction, U can become negative and lead to formation of bipolarons. $V = A/R_{ij}$ is the Coulomb energy of the two polarons occupying site i and j before they form a bipolaron. It should be subtracted from the Hubbard energy. The last two terms refer to spin transport due to spin exchange.

It is well known that charge transport in a disordered organic system can be modeled in terms of percolation theory in the spirit of Miller and Abrahams [10,11]. However, the spin transport itself can form a percolation path [12]. To simplify the problem of Eq. (1a), we simulate the spin transport based on a connected percolation model. Spin transport, carried by polarons hopping or spin exchange, can be seen as a network of random spin-resistors. For polaron hopping, the spin-resistors R_{sij} between two sites i and j, can be considered as a network of random resistors, the respective resistors being $R_{sij} = 1/W_{i\to j}$ and $R_{sij} = 1/\eta_{i\to j}$. This model is schematically shown in Fig. 1.

If the initiated site is fixed, every target site can be characterized by parameter R, and the rate of spin transport can then be written in terms of the parameter R, as follows in Eq. (3). The rate of spin transport $v_{ij} = v_0\exp(-R)$ is a function of R and decreases with increasing R. That is, the rate of spin transport decreases with increasing the distance between two sites R_{ij} and increases with increasing temperature.

$$R = \begin{cases} \left.\begin{matrix} 2\alpha(1+\beta\cos\theta)R_{ij} + \frac{E_j-E_i}{k_BT}\ \ E_j > E_i - 2\alpha\beta\cos\theta \\ 2\alpha R_{ij}\ \ E_j < E_i - 2\alpha\beta\cos\theta \end{matrix}\right\}\text{hopping to empty states} \\ \left.\begin{matrix} 2\alpha(1+\beta\cos\theta)R_{ij} + \frac{E_j-E_i+U-\mathrm{V}}{k_BT}\ E_j > E_i - 2\alpha\beta\cos\theta - U + V \\ 2\alpha(1+\beta\cos\theta)R_{ij}\ E_j < E_i - 2\alpha\beta\cos\theta - U + V \end{matrix}\right\}\text{bipolaron formation} \\ 2\alpha R_{ij} - \log\left(\frac{0.821\frac{q^2\alpha}{\varepsilon\hbar}(2\alpha R_{ij})^{\frac{5}{2}}}{v_0}\right)\ \text{spin exchange} \end{cases} \cdot \tag{3}$$

As $R = R_{nn}$, the infinite percolation cluster of interconnected bonds is approached, which is responsible for the spin transport in a disordered system. Thus, the critical value R_{nn} will determine the temperature, electric field, and magnetic field dependence of spin transport coefficients. According to the percolation theory, the infinite cluster is established when the average number of bonds per site attains the critical value of B_c. For three dimensional amorphous systems, the value of B_c is given by 2.8 [13]. Based on our previous work [14,15], the percolation criterion B_c of spin transport can be written as

$$\begin{aligned} B_c = \frac{1}{8\alpha^3}\Bigg[&\int_0^\pi \sin\theta d\theta \int_0^{R_{nn}} 2\pi r^2dr \int_{-\infty}^{R_{nn}+\epsilon_i-r(1+\beta\cos\theta)} \frac{g(\epsilon)}{1+\exp(\epsilon-\epsilon_F)}d\epsilon \\ &+ \int_0^\pi \sin\theta d\theta \int_0^{R_{nn}} 2\pi r^2dr \int_{-\infty}^{R_{nn}+\epsilon_i-r(1+\beta\cos\theta)-u+V} \left(\frac{\frac{1}{4}g(\epsilon)}{1+\exp(\epsilon-\epsilon_F)} + \frac{\frac{3p}{4}g(\epsilon)}{1+\exp(\epsilon-\epsilon_F)}\right)d\epsilon \\ &+ \int_0^{R_{nn}} 2\pi r^2dr \int_{-\infty}^{\infty}\left(\frac{\frac{\eta_{i\to j}}{4}g(\epsilon)}{1+\exp(\epsilon-\epsilon_F)}\right)d\epsilon\Bigg]. \end{aligned} \tag{4}$$

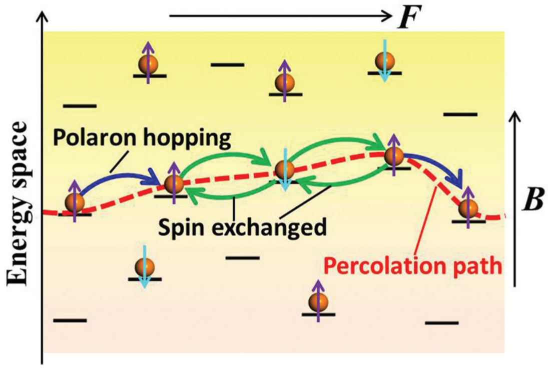

FIG. 1. (Color) Schematic picture of spin percolation transport in organic semiconductors. Purple arrows: spin up; blue arrows: spin down; cyan arrow lines: polaron hopping transport; mazarine arrow lines: spin exchanged transport; red dotted lines: percolation path.

Note that we use normalized coordinates here ($\epsilon_i = E_i/k_BT$ and $r = 2\alpha R_{ij}$) and that ϵ_F denotes the Fermi level, where the first part in the bracket refers to the spin carried by polaron hopping and the second part to spin exchange. $g(\epsilon)$ is density of states (DOS). In organic semiconductors, the variations of site energies due to disorder are usually assumed to be Gaussian type. This holds for spin transport in disordered organic semiconductors as well [7]:

$$g(\epsilon) = \frac{N_t}{\sqrt{2\pi}\sigma}\exp\left(-\frac{\epsilon^2}{2\sigma^2}\right), \tag{5}$$

where σ is the width of energy disorder and N_t is the total localized states density. Using Gaussian DOS and Fermi-Dirac distribution, the carrier concentration in the disordered system can be evaluated as

$$n = \int_{-\infty}^{\infty} \frac{g(\epsilon)}{1+\exp(\epsilon-\epsilon_F)}d\epsilon. \tag{6}$$

Consider a simple case, that is, the magnetic field is perpendicular to the electric field. Then, the spin flow due to either polaron hopping or spin exchange occurs in the same direction (for example, x). In organic semiconductors, the localized states randomly distributed in energy and space to form a discrete array of sites in the hopping space. The most probable hop for a spin polarization on a site at a particular energy ϵ_i is to the empty site or filled site with opposite spin at closest range R_{nn}, which can be evaluated from Eq. (4). The average transport distance along the electric field F is $\overline{x_f}$ (the detailed derivation of $\overline{x_f}$ is based on our previous work [15]). If one knows the average transport distance and considers that the average rate of the spin transport is $v_0\exp(-R_{nn})$, the diffusion coefficient of spin migrating at energy ϵ_i becomes

$$D(B,\epsilon_i,U) = \frac{\overline{x_f^2} - \overline{x_f}^2}{6/(v_0\exp(-R_{nn}))}. \tag{7}$$

After averaging over the normalized site energies, we end up with

$$D(B,F,T,\epsilon_F,U) = \frac{\int_{-\infty}^{\infty} g(\epsilon_i)/[1+\exp(\epsilon_i-\epsilon_F)]D(B,\,\epsilon_i,U)d\epsilon_i}{\int_{-\infty}^{\infty} g(\epsilon_i)/[1+\exp(\epsilon_i-\epsilon_F)]d\epsilon_i}. \tag{8}$$

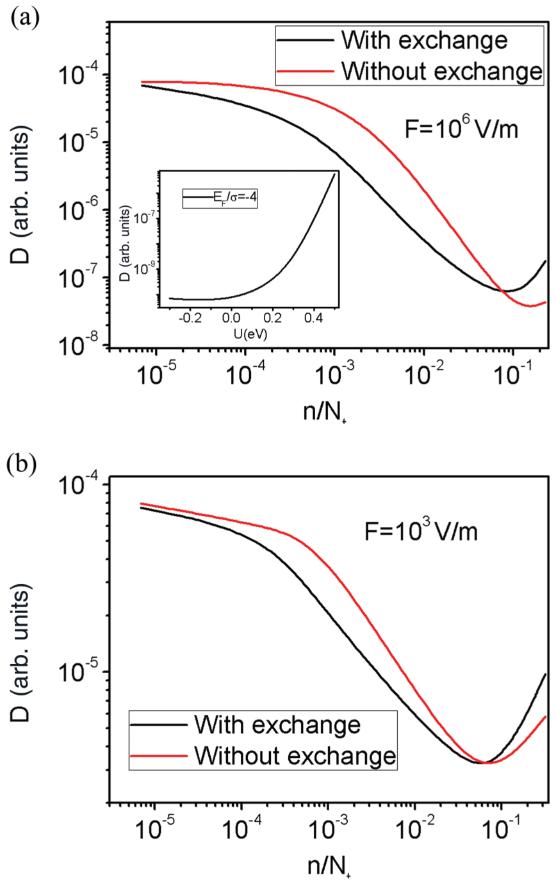

FIG. 2. (Color) (a) Carrier density dependence of spin diffusion coefficient at high electric field (inset: U dependence of spin diffusion coefficient); (b) carrier density dependence of spin diffusion coefficient at low electric field.

III. RESULTS

In Fig. 2(a), we display the comparison between the theoretical calculation for density dependence of D with and without spin exchange. We find that in the regime of high charge carrier density regime, both spin exchange and spin carrier by polaron hopping will increase with carrier density, being similar to the density dependence found by Ref. [4]. However, at variance with the prediction in the prediction from Ref. [4] where D keeps the constant at low density, here D will decrease with carrier density at the low carrier density regime. The discrepancy between our calculation and Ref. [4] is due to the fact that D itself is carrier density dependent [11,15]. This has not been taken into account in Ref. [4]. Note, low carrier density regime is more realistic for organic spin valve.

Another interesting property from Fig. 2 is that the spin exchange will decrease the diffusion coefficient. The fact that D decreases with carrier density at high field is associated with deep tail states of the DOS. The reason is that deeply trapped spins are more almost immobile. Therefore, they lag behind the packet of moving spins. Eliminating those deep states by increasing the carrier density must therefore reduce field assisted diffusion [15]. In this situation, spin exchange will hinder filling of the deep states and decreases the diffusion coefficient. The parameters used for calculation here are

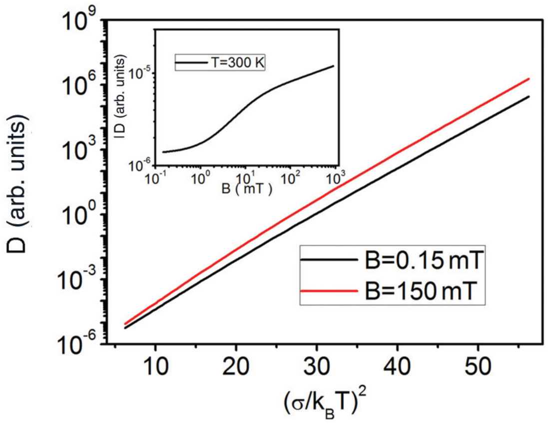

FIG. 3. (Color) Temperature and magnetic field dependence of diffusion coefficient.

$N_t = 1 \times 10^{28}\,\mathrm{m}^{-3}$, $a^{-1} = 8\,\text{Å}$, $U = 0.5\,\mathrm{eV}$, $\sigma/k_BT = 2.5$, $B = 0.15\,\mathrm{mT}$, $A = 0.24$, $v_0 = 1.76 \times 10^{10}\,\mathrm{s}^{-1}$, $a_{\mathrm{eff}}/v_0 = 1$, and $\gamma_e = 0.176\ \mathrm{ns}^{-1}\mathrm{mT}^{-1}$. These values are characteristic for organic semiconductors [7,8]. Furthermore, Fig. 2(a) shows that the spin diffusion will increase with U. The reason for this result might be as follows. For the positive U, the increase of U will facilitate the deep trap filling and leads to the increase of D. However, for the negative U, this effect will be weak, and D will stay as constant.

The effect of deep states on spin diffusion is also diminished by raising the temperature, as shown in Fig. 3. The parameters used here are the same as those in Fig. 2. D approaches an exponential dependence on $(\sigma/k_BT)^2$. This type of dependence on the disorder parameter is a characteristic feature of hopping transport within a Gaussian DOS. It can also be seen that D will increase with the magnetic field. Physically, spin precession is envisioned as percolation of spin transport through the unblocked sites f_{ub} (empty states or filled states with opposite spin). A magnetic field will increase the fraction of the unblocked site, $f_{ub} = 1 - f_b$, by spin flip and, thus, increases spin diffusion in the regime of low carrier density. This effect will disappear when B becomes comparable or larger than the hyperfine field (see insert in Fig. 3) [8].

In what follows, we want to compare the calculation to the experimental data. Until now, the direct experiment for spin diffusion coefficient is still very scarce; however, the spin diffusion length has been measured by some groups. To relate the spin transport to the spin diffusion length, we follow the definition in Ref. [16]. The spin diffusion length as a function of site energy ϵ_i is given as

$$L(\epsilon_i) = \sqrt{D(\varepsilon_i)\tau(\varepsilon_i)} = \sqrt{\frac{\overline{x_f^2} - \overline{x_f}^2}{6}}, \tag{9}$$

where $\tau(\varepsilon_i) = 1/v_0 \exp(-R_{nn})$ is the carrier lifetime. To determine the average spin diffusion length in the system, we average $L(\epsilon_i)$ over energy as

$$L = \frac{\int_{-\infty}^{\infty} g(\epsilon_i)/[1 + \exp(\epsilon_i - \epsilon_F)]\mathrm{L}(\epsilon_i)d\epsilon_i}{\int_{-\infty}^{\infty} g(\epsilon_i)/[1 + \exp(\epsilon_i - \epsilon_F)]d\epsilon_i}. \tag{10}$$

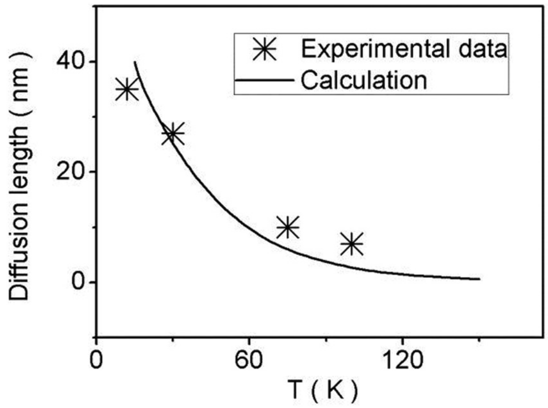

FIG. 4. Comparison between the theoretical calculation and experimental data. Symbols: experimental data from Ref. [6]. Lines: fits using the theoretical model given by Eq. (10). The parameters used for calculation are $v_0 = 1.67 \times 10^{10}\,\mathrm{s}^{-1}$, $a_{\mathrm{eff}}/v_0 = 1$, $\sigma/k_BT = 1.78$, $B = 0.29\,\mathrm{mT}$, $a^{-1} = 1.5\,\text{Å}$, and $U = 0.5\,\mathrm{eV}$, and the other parameters are the same as those in Fig. 2.

Using Eq. (10), we calculate the temperature dependent spin diffusion length and compare it to the experimental data from Ref. [6], as shown in Fig. 4. In this experiment, a new depth-resolved technique was used to measure the spin polarization of current-injected electrons in an organic spin valve. The temperature dependence of the spin diffusion length was then obtained. It can be seen that the diffusion length will decrease with the increase of temperature. Generally, for regular hopping transport the diffusion length of carrier always increases with the increase of temperature because the carrier transport is thermally activated and the increasing temperature will facilitate carrier hopping. However, when applying an electrical bias field in an organic device, the spin packet will be broadened by field assisted diffusion [15,17,18]. Since this effect depends on state filling, the diffusion length will decrease with increasing temperature, as discussed in relation to Fig. 3. This explains the result of the experiment from Drew *et al.* [6], where the diffusion length was measured under a strong bias field. In this context, it is worth noting that Yu [16] assumes that the hopping rate is determined by the Coulomb gap and disregards energy fluctuations, implying a decrease of the hopping rate with increasing temperature. This is in disagreement with the current paper.

We note that the experiment in Ref. [6] was measured at a higher voltage, which validates our assumption here. We also note that Yu has explained this experimental data by assuming that the hopping rate is determined by Coulomb gap [16]. We are afraid that this assumption is inappropriate for organic semiconductors.

IV. CONCLUSIONS

We developed a theoretical framework for spin transport based upon percolation and hopping theories. It describes the dependence of spin transport as a function of temperature and both the electric and magnetic field parametric in the Hubbard energy of charge carrier pairs. We find that, in disagreement with an earlier prediction [16], in an organic spin valve, spin exchange will hinder spin transport.

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