

## Spin-Flip Induced Magnetoresistance in Positionally Disordered Organic Solids

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A model for magnetoresistance in positionally disordered organic materials is presented and solved using percolation theory. The model describes the effects of spin dynamics on hopping transport by considering changes in the effective density of hopping sites, a key quantity determining the properties of percolative transport. Faster spin-flip transitions open up “spin-blocked” pathways to become viable conduction channels and hence produce magnetoresistance. Features of this percolative magnetoresistance can be found analytically in several regimes, and agree with previous measurements, including the sensitive dependence of the magnetic-field dependence of the magnetoresistance on the ratio of the carrier hopping time to the hyperfine-induced carrier spin precession time. Studies of magnetoresistance in known systems with controllable positional disorder would provide an additional stringent test of this theory.

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Spintronics [1] in organic materials has generated considerable interest in recent years [2] due to the long spin lifetimes of organic semiconductors as well as the flexibility, low cost, and chemical tunability of organic devices [3]. Spin transport properties are intimately connected to the electrical transport properties [4], so although spin transport through inorganic semiconductors has been extensively explored [5,6], novel features should be expected in organics due to their very different electronic transport properties. The understanding of spin transport in organics has been challenged by the discovery of magnetic field effects on properties such as conductivity and electroluminescence [7–15], and characterized by magnetoresistances of 10%–20% in magnetic fields as small as 10 mT. Several new models of organic magnetoresistance (OMAR) have been proposed, many of which involve spin-dependent processes emanating from hyperfine interactions. These models can be broadly categorized by their reliance on bipolaron [13] or electron-hole pair [9,10] formation rates, and their dependence on the relative spin of two carriers located at neighboring sites. However, no model of OMAR has explicitly taken into account how the presence of spin-blocked sites affects the theoretical description of hopping transport for a single carrier using percolation theory [16,17].

This Letter provides a description of magnetoresistance (MR) based on percolative hopping transport for positionally disordered organic semiconductors. The theory proposed here maps the complex phenomena of spin-dependent hopping onto a simple problem of  $r$  percolation with an effective density of hopping-accessible sites that depends on the magnetic field through spin relaxation. We focus on unipolar charge transport since several analytic results can be readily obtained; an extension to bipolar transport can be done with similar techniques. Our percolation-based theory allows us to explain the width and saturation of measured MR curves [12,18,19], as well

as make predictions of MR in systems with low site concentration and high temperatures. This approach is superior to an analytic analysis of the resistance determined by a single “bottleneck” pair of sites [20], because (1) our theory is not limited to slow carrier hopping, (2) our analysis does not require a very large electric field to force hopping in a single direction, and (3) in our analysis percolation theory, rather than a phenomenological branching parameter, determines the resistance for carriers to go around the bottleneck pair if the bottleneck resistance becomes too large. Finally, we propose additional experiments that could test our theory and thereby shed light on the operative mechanisms leading to OMAR. This approach can be generalized to systems with both positional and energetic disorder, and similar MR results and trends are expected, although analytic results may no longer be possible. We note some of our results are reproduced by recent numerical simulations [21].

*Model.*—We model the spatially disordered organic system as a network of random resistors in the spirit of Miller and Abrahams [22]. The resistance between two sites,  $i$  and  $j$ , is given by  $R_{ij} = R_0 e^{2r_{ij}/a}$  where  $r_{ij}$  is their separation and  $a$  is the localization length of a carrier at a site which we assume to be constant throughout the system. The bulk resistance in such a random resistor network is known from percolation theory [16,23,24]. The bulk resistance is governed by a critical resistance (distance)  $R_c$  ( $r_c$ ) which is the smallest resistance (or equivalently the smallest separation) that still allows for an infinitely large network of bonds. This percolation length is set by the bonding criterion:

$$B_c = 4\pi \int_0^{r_c} r^2 N dr, \quad (1)$$

where  $N$  is the density of sites in the system and  $B_c$  is a number that determines how many bonds each site in the percolating network must connect to on average;  $B_c \approx 2.7$

in three dimensions [16]. Energy disorder can be neglected in transport calculations when the intersite separation is large and temperatures are high; conductivity due to  $r$  percolation has been observed in organic semiconductors in this regime [25,26]. These conditions are assumed throughout this Letter.

Spin affects electronic transport in hopping transport through the Pauli exclusion principle, as shown schematically in Fig. 1; double occupation of carriers on a single site is forbidden if their spins are parallel (P), but allowed if they are antiparallel (AP) [13,27] (at the cost of a Coulomb interaction energy  $U$ ). A carrier with arbitrary spin is restricted from hopping to an occupied site with P spin but may hop to a site occupied by an AP spin just as it would to an unoccupied site. Handling the effect of the Coulomb interaction energy  $U$  in the  $r$ -percolation regime requires some care. Including  $U > 0$  provides a charge-blocking effect that quenches spin-flip effects, because a carrier cannot effectively hop from one singly occupied state onto a second, creating a doubly occupied state. In the more general situation of energy disorder this unphysical charge-blocking effect is removed if the width of the energy distribution of the hopping sites is larger than or comparable to  $U$  (commonly the case). In this situation, frequently a carrier can hop from one singly occupied state to a second, because the energy of the two carriers on the same lower-energy site is still lower than the energy of the two carriers on two separate sites. Thus, theory for MR in the variable range hopping regime, in which there is energy disorder, suggests that  $U > 0$  produces larger MR [28] than  $U = 0$ . It is therefore the case that the more physical regime for positional disorder is to take  $U = 0$  to avoid an unphysical excessive charge-blocking effect, and we make that assumption. The respective concentrations of the three types of sites (parallel, antiparallel, and unoccupied) are  $N_P$ ,  $N_{AP}$ , and  $N_0$ . We consider carrier

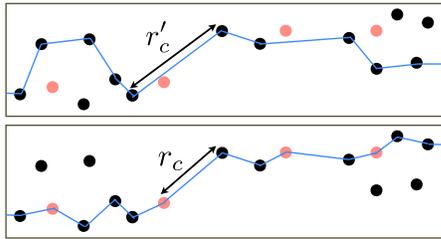


FIG. 1 (color online). Spin blocking in transport. Black sites, with density  $N'_{\text{eff}}$ , are accessible sites for a carrier spin starting on the left and proceeding to hop to the right along a sequence of nearest-neighbor sites. Top: Red (gray) sites are inaccessible due to spin blocking (as described in main text). The path traversed (blue line) has a longest hop, over a distance  $r'_c$ , which determines the resistance. Bottom: When spin-flips are permitted, some red (gray) sites become accessible and the total density of accessible sites is  $N_{\text{eff}} > N'_{\text{eff}}$ . The carrier's path is dramatically altered; the average intersite separation decreases, as does  $r_c$ .

concentrations dilute enough to neglect hops to doubly occupied sites.

Since carrier hopping to an occupied site with a P spin is forbidden, the concentration of sites in Eq. (1) is effectively reduced to  $N - N_P$ . In the absence of spin flips we would then write the bonding criterion as  $B_c = 4\pi \int_0^{y_c} r^2 N'_{\text{eff}} dr$ , where  $N'_{\text{eff}} = N - N_P$ . The spin flip of a carrier at a site can be understood as a dynamical process that will cause the relative spin orientation between two singly occupied sites to change. Hence, the hopping dynamics between two occupied sites is strongly dependent on spin flips. If the total concentration of singly occupied sites is fixed at  $N_s$ , then at any given time the average densities of P-spin and AP-spin sites are  $N_s/2$ . Thus, as a carrier attempts a hop to a singly occupied site, the probability of success will be  $1/2$ , independent of spin effects. The density of sites for these successful hops is  $N_{AP} = N_s/2$ . So as before, the density of unrestricted hopping sites is  $N'_{\text{eff}}$ . The hopping attempt is foiled when the singly occupied site is inhabited by a parallel spin, which occurs at  $N_P = N_s/2$  sites.

We assert that the spin-blocked path can be opened by any process that alters the relative spin orientation between the two sites. The probability for the blockade to be lifted by the time the next hopping attempt takes place,  $\tau_h$ , is  $p$ . We thus modify the effective density of P sites to be  $[1 - p]N_P$ . The resulting modification of the density of sites that can be hopped to,  $N_{\text{eff}}$ , accounts for the possibility of spin flips of spins located at singly occupied sites. We write the bonding criterion as

$$B_c = \frac{4}{3}\pi a^3 y_c^3 (N - N_P) + 4\pi a^3 N_P \int_0^{y_c} y^2 p dy, \quad (2)$$

where  $y_c = r_c/a$  is the dimensionless critical length which dictates the threshold resistance  $R_c = R_0 e^{2y_c}$ ;  $\tau_h = v_0^{-1} e^{2y}$  is the hopping time. A quantity  $y_{c_0} = (3B_c/4\pi a^3 N)^{1/3}$  is defined as the critical intersite spacing in the absence of all spin effects. In general,  $y_c$  cannot be isolated in Eq. (2) and the resultant MR can only be obtained numerically; however, in the dilute carrier regime ( $N_P \ll N$ ), the MR obeys the analytic expression

$$\text{MR} \approx 2 \frac{1}{y_{c_1}^2} \frac{N_P}{N} \int_0^{y_{c_1}} y^2 [p(0) - p(H)] dy, \quad (3)$$

where  $y_{c_1} = y_{c_0} (1 - N_P/N)^{-1/3}$  is the renormalized critical intersite spacing. The MR scales linearly with the fraction of singly occupied sites.

Most of the results reported below are based on the form of  $p$  that is appropriate if the spin flips in these organic materials are caused by the hyperfine interaction (HI) [9,13]; expressions and implications appropriate for spin flips caused by the spin-orbit interaction are summarized briefly at the end of this Letter. Figure 2 emphasizes the main results of our theory. Panel (a) shows our calculations of MR for three different organic semiconductors: the small molecule trinitro-9-flourenone (TNF) which has

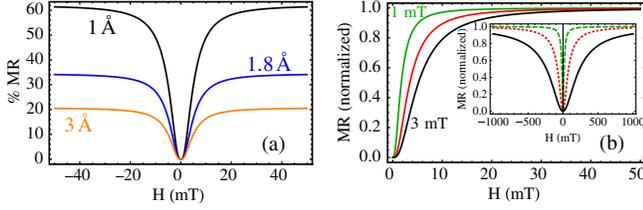


FIG. 2 (color online). (a) Calculated MR %, using the hyperfine averaged version of Eq. (7) for a polymer PPV derivative (orange bottom line) with localization length  $a = 3 \text{ \AA}$  [39], the small molecule TNF (blue middle line) with localization length  $a = 1.8 \text{ \AA}$  [25], and a generic organic material (top black line) with localization length  $a = 1 \text{ \AA}$ . The total site density is  $N = 10^{26} \text{ m}^{-3}$  and the singly occupied site density is  $N_p = 10^{25} \text{ m}^{-3}$ . (b) Calculated normalized MR, as in (a), at three different hyperfine field distribution widths ( $h_I$ ). The middle curve (red line) is for 2 mT. Inset: Normalized MR, using Eq. (5), for generic organic material at total site densities corresponding to  $\tau_c \approx 0.5 \text{ ns}$  (green dashed line),  $\tau_c \approx 0.1 \text{ ns}$  (red dotted line),  $\tau_c \approx 0.05 \text{ ns}$  (black solid line). Only HI is assumed; unless noted otherwise, all figures use  $h_I = 1 \text{ mT}$  and  $v_0 = 10^{12} \text{ s}^{-1}$ .

electrons as carriers (blue middle line), the polymer derivative of polyphenylene vinylene (PPV) (orange bottom line) with hole carriers, and a generic material (black top line) that possesses a smaller localization length ( $1 \text{ \AA}$ ) than the other two ( $1 \text{ \AA} < a_{\text{TNF}} < a_{\text{PPV}}$  as given in figure caption). This result suggests that organic materials with small localization lengths yield the largest MR. As an increasing bias voltage tends to increase the localization length, for our theory the MR will decrease as the bias is increased. Experimental observations of the bias dependence are ambiguous, which may be due to the bias dependence of the majority and minority current injection rates for a bipolar organic device. Panel (b) compares our calculations for slow hopping (main) and fast hopping (inset). The MR width for slow hopping is set by the hyperfine fields, whereas the width for fast hopping is set by the hopping rate. These results are derived and discussed in the remaining portion of this Letter.

*Fast hopping.*—When hopping is faster than the hyperfine precession frequency, the carrier spin experiences a random field for the short duration of time that it resides at a site. The spin-flip rate is identical to the well-known spin relaxation rate from HI in the motional narrowing regime [29]:

$$\frac{1}{\tau_s} = \frac{v^2}{v_H^2 + \tau_h^{-2}} \frac{1}{\tau_h}. \quad (4)$$

$v_H$  and  $v$  are precession frequencies due to the external field  $H$  and the in-plane internal hyperfine fields, of strength  $h$ . The probability for the P-spin to flip at the next hop is  $p(\tau_s) = 1 - e^{-\tau_h/\tau_s}$ , which will permit a hop to the target site. This is a condition met in part when the density of sites is high. In this case, the probability for a

spin flip is  $p(\tau_s) \approx \tau_h/\tau_s$ . The hyperfine fields are random at each site so a correct description of the MR involves an average over the Gaussian distribution of these fields. The resulting MR response, for  $y_{c1} \gg 1$ , averaged over the Gaussian distribution of hyperfine fields with width  $h_I$ , is

$$\langle \text{MR} \rangle = \frac{1}{2} \frac{N_p}{N} v_I^2 \tau_c^2 \left[ 1 - \frac{1}{v_H^2 \tau_c^2} \ln(1 + v_H^2 \tau_c^2) \right], \quad (5)$$

where  $\tau_c$  is the hopping time at the critical radius and  $v_I$  is the precession frequency corresponding to the field  $h_I$ . The positive MR can be understood by considering the field dependence of the relaxation mechanism; e.g., an increasing field *suppresses* spin relaxation via HI which makes the spin blockade more effective. The dependence of MR on the magnetic field here is identical to an earlier calculation for amorphous semiconductors performed in the fast hopping limit [28].

*Slow hopping.*—The condition  $1/v_I \gg \tau_h$  may not always be suitable for organic systems since the mobilities are low. As site separations increase, the carrier hopping rate is reduced to  $1/v_I < \tau_c$ . During the requisite waiting time to hop, the carrier spin at  $i$  and target-site spin at  $j$  experience the applied field and their respective hyperfine fields  $h_i$  and  $h_j$ . Given two spins initially P aligned, the different hyperfine fields at the two sites rotate the spins to produce the possibility of AP alignment. We interpret this as a spin flip at either site. The time-averaged probability that the next hop is successful is  $p(H) = p_{ij} + p_{ji}$  where  $p_{ij}$  is the probability for the carrier at site  $i$  to be opposite its initial state while the carrier at site  $j$  remains in its initial state [30,31]:

$$p_{ij} = \frac{1}{2} \frac{h_i^2}{h_i^2 + H^2} \left[ 1 - \frac{1}{2} \frac{h_j^2}{h_j^2 + H^2} \right]. \quad (6)$$

The second term,  $p_{ji}$  is the reverse possibility. The MR, from Eq. (3), is ascertained to be

$$\text{MR} \approx \frac{1}{3} y_{c1} \frac{N_p}{N} \frac{H^4}{(h_i^2 + H^2)(h_j^2 + H^2)} \quad (7)$$

prior to the average taken over the hyperfine field distribution. We note that the MR is independent of the hopping rate, which contrasts starkly with the fast hopping case.

*MR line shape.*—Two characteristic features to quantify MR are its value at high magnetic fields,  $\text{MR}_{\text{sat}}$ , and its width  $\delta$ , which we define as the half-width at half-maximum. Figure 3 shows that a crossover from slow to fast hopping exists for both the saturated MR and MR width. Slow hopping, which for instance could result from large intersite distances, is conducive to large values of MR. The formula for  $\text{MR}_{\text{sat}}$  in the low site density regime, derived from Eq. (7), is

$$\text{MR}_{\text{sat}} \approx \frac{1}{3} y_{c0} \frac{N_p}{N}. \quad (8)$$

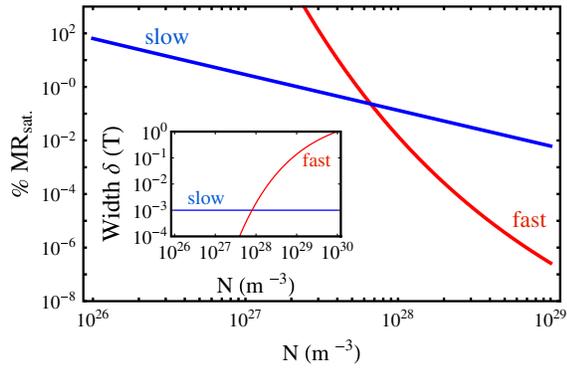


FIG. 3 (color online). Percentage saturated MR versus site concentration  $N$ . The slow hopping curve (blue) uses Eq. (8) and is valid for low  $N$ ; fast hopping (red), valid at high  $N$ , uses the high field limit of Eq. (5) with  $h_I = 1$  mT,  $v_0 = 10^{12}$  s $^{-1}$ ,  $a = 1$  Å, and  $N_p = 10^{25}$  m $^{-3}$ . Inset: MR width  $\delta$  as a function of site concentration for the same parameters.

Remarkably, the saturated MR is independent of HI. We note that in the deuterated PPV experiments of Ref. [18],  $\delta$  of the magnetoluminescence decreased when the hyperfine field was reduced whereas the high field magnetoluminescence was nearly unchanged. This result is consistent with our theory. In the fast hopping limit, the site concentration dependence is even stronger since  $\text{MR}_{\text{sat}}$  contains an exponential dependence on  $N$  through  $\tau_c$ . The MR widths also take on very different behaviors which are discerned from their MR expressions above [Eqs. (5) and (7)]. In the fast hopping region, the width is *independent* of the hyperfine interaction but strongly dependent on the hopping rate. Note that the width for fast hopping is larger—this is due to the quicker hopping rate which results in greater fields being required to suppress HI spin relaxation. MR widths as large as 40 mT—much greater than the hyperfine fields present—have been measured [12,19]; our theory suggests these large widths are related to the hopping rate and not the hyperfine field. Often it has been assumed [18,20,32] that  $\delta$  must depend on  $h_I$ . We find that this is only true in the slow hopping case. We also note that a similar dependence of line shape width on hopping was seen in recent numerical simulations [21].

The MR we calculate for fast and slow hopping are fit well [33] by Lorentzian functions but not by an alternate, proposed non-Lorentzian function [34]. Both forms have been experimentally observed [34]. A fit to Gomez’s hole-only data [19], where the MR width is over 25 mT, yields a value of  $\tau_c = 0.2$  ns which is consistent with the regime where  $\tau_c$  is much smaller than the hyperfine period (here  $\sim 6$  ns).

*Spin-orbit coupling effects.*—For fast hopping, our theory is quite general in that any spin relaxation mechanism can be included for  $\tau_s$ . Here we consider the influence of spin-orbit coupling (SOC); a recent calculation of SOC in several organic solids suggests that SOC may be significant [35]. Additionally, SOC manifests itself by producing

inhomogeneous g-factors (IG). The result of SOC produces a spin relaxation rate:  $\tau_s^{-1} = [b^2 v_H^2 (v_H^2 + \tau_h^{-2})^{-1} + \gamma^2] \tau_h^{-1}$ , where  $\gamma$  determines the SOC strength,  $b = \sqrt{3/10} \delta g$ , and  $\delta g$  is known to be proportional to  $\gamma$  [29]. The field-independent portion reduces the total MR by  $e^{-\gamma^2}$  but leads to no other qualitative change. This result is expected since SOC is field-independent and has been observed in Alq $_3$  doped with Iridium [9]. IG, which increases with an increasing field, leads to negative MR:  $-\frac{1}{2} \times \frac{N_p}{N} b^2 \ln(1 + v_H^2 \tau_c^2)$ , where  $(v_I + v_H) \tau_c \ll 1$ . At low fields, this effect is expected to be small compared to HI-induced MR. Recently, IG was studied in the slow hopping regime [36] but  $\delta g$  was found to be unrealistically high to explain the magnetic field effects [15].

The prediction of large MR in the slow hopping regime necessitates measurements over a controlled and wide range of site concentrations. For our  $r$ -percolation theory to be valid, the unipolar organic device must possess a low density of molecular sites and this density must be controllable. Conduction via  $r$  percolation was identified in TNF films by measuring the electron mobility through time-of-flight experiments [25,26]. The molecular density of TNF could be carefully controlled by dispersing TNF in a polyester host that did not alter the transport properties. We suggest similar experiments to look for the magneto-resistive dependences on the hopping rate described in this Letter. We conclude by noting that this theory has implications for MR effects in amorphous semiconductors [29] and colloidal quantum dots [37], as well as for spin diffusion in organic spin valves [38].

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