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Theory for Spin Diffusion in Disordered Organic Semiconductors

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We present a theory for spin diffusion in disordered organic semiconductors, based on incoherent hopping of a charge carrier and coherent precession of its spin in an effective magnetic field, composed of the random hyperfine field of hydrogen nuclei and an applied magnetic field. From Monte Carlo simulations and an analysis of the waiting-time distribution of the carrier we predict a surprisingly weak temperature dependence, but a considerable magnetic-field dependence of the spin-diffusion length. We show that both predictions are in agreement with experiments on organic spin valves.

The study of electron-spin transport through nonmagnetic spacer materials in between ferromagnetic electrodes is an extremely active field, because of the rich physics involved and the important applications in the area of magnetic sensors [1]. If the spin-diffusion length is larger than or comparable to the distance between the electrodes, the current through such structures depends strongly on the mutual orientation of the magnetizations of the electrodes, which is called the spin-valve effect, leading to "giant magnetoresistance" (GMR) [2,3].

Traditionally, nonmagnetic metals are used as the spacer-layer material in these structures. Spintronic devices utilizing spin injection and transport through a *semiconducting* spacer layer offer additional functionalities, such as spin transistors and the possibility to realize quantum computation logic. Consequently, much effort is put into finding suitable materials. Spin relaxation in the inorganic materials traditionally used in these structures, containing relatively heavy atoms, is mainly caused by spin-orbit coupling [4]. Organic semiconductors (OS) are a very interesting alternative because of the enormous versatility of organic chemistry and because the light atoms from which they are composed cause very little spin-orbit coupling [5]. Recent years have seen the first demonstrations of GMR devices [6–12] as well as magnetic tunnel junctions [13] using OS as spacer layer. Here we will investigate the former type of devices. The experiments reported so far have shown that when the thickness of the OS spacer layer increases, the GMR effect in these devices disappears on a typical length scale of the order of 10–100 nm. Two very important and still unanswered questions, addressed in this Letter, are what is the cause of the remaining spin relaxation and what factors determine the spin-diffusion length?

Recent research on magnetic-field effects on the resistance and luminescence of OS has led to the conclusion that the hydrogen hyperfine fields are involved, influencing reactions between spin-carrying radicals (polarons, triplet excitons) [14–17]. The accurate prediction of magnetore-sistance line shapes assuming coupling of the spin to these hyperfine fields [17] strongly suggests that this coupling is the main source of spin relaxation in OS. In this Letter, we take this as our working hypothesis. Since typically many (~10 or more) hydrogen nuclear spins couple to the spin of a charge carrier in OS, we can replace the hyperfine coupling by a classical, quasistatic, and random field, distributed according to a three-dimensional Gaussian [18], with standard deviation $B_{\rm hf}$. In addition, we model charge transport in disordered OS by hopping of carriers between localized sites with random site energies, distributed according to a Gaussian density of states (GDOS) with standard deviation σ [19]. Hence, we describe spin diffusion in these materials by a combination of *incoherent* hopping of a carrier in a GDOS together with *coherent* precession of its spin $\mathbf{S}(t)$ around a local effective magnetic field; see Fig. 1(a). At each hopping site i this effective field is $\mathbf{B}_i = \mathbf{B}_{{\rm hf},i} + \mathbf{B}$, where $\mathbf{B}_{{\rm hf},i}$ is the random hyperfine field at this site and $\mathbf{B} = B\hat{\mathbf{z}}$ the externally applied magnetic field, e.g., the field to which a GMR sensor should respond. With typically $B_{\rm hf} \approx 5$ mT the hyperfine precession frequency is $\omega_{\rm hf} = \gamma B_{\rm hf} \approx 10^8$ s^{-1} (γ is the gyromagnetic ratio).

We consider the situation that a carrier with unit charge e (electron or hole) and spin fully polarized in the z direction is injected by an electrode into the organic material at $x = 0$ and moves to the opposite electrode under the influence of an electric field $\mathbf{E} = E\hat{\mathbf{x}}$. We assume that nearest-neighbor hopping takes place by thermally assisted tunneling [20] from site i to j with a rate $\omega_{ij} = \omega_{\rm hop} \exp[-(\varepsilon_j - \varepsilon_i)/k_B T]$ for $\varepsilon_j \geq \varepsilon_i$ and $\omega_{ij} = \omega_{\rm hop}$ for $\varepsilon_j < \varepsilon_i$, where T is temperature, k_B is Boltzmann's constant, and ε_i and ε_j are the on-site-energies of sites i and j, with a contribution due to the electric field added. The prefactor $\omega_{\rm hop}$ contains a phonon attempt frequency as well as a factor related to a wave function overlap. For hopping in disordered OS at not too low temperatures it is a good approximation to include only nearest-neighbor hopping [21]. Furthermore, it has been shown that positional disorder is much less important than energetic disorder [19], so for simplicity we neglect
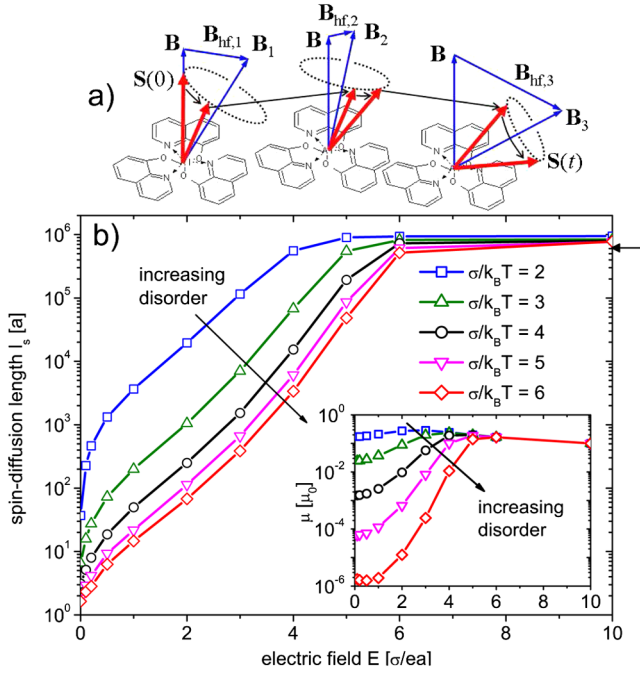
FIG. 1 (color online).   (a) Mechanism for spin diffusion, in this case for the molecular semiconductor Alq_3. (b) Spin-diffusion length l_s [as multiples of the lattice constant] vs electric field E at zero magnetic field, for $r \equiv \omega_{hop}/\omega_{hf} = 1000$ and different $\hat{\sigma} \equiv \sigma/k_B T$. The arrow at the right axis indicates the result for a one-dimensional chain at large E. Inset: corresponding mobility μ vs E, in units of $\mu_0 \equiv ea^2\omega_{hop}/\sigma$.

positional disorder and take a fixed nearest-neighbor distance a.

Clearly, the ratio $r \equiv \omega_{hop}/\omega_{hf}$ is an important parameter. If r is large the influence of the hyperfine field is small and large spin-diffusion lengths can be expected, while the opposite holds if r is small. For derivatives of the familiar π-conjugated polymer poly-(*para*-phenylene vinylene) (PPV) we obtain an estimate of 10^9–10^{11} s^{-1} for ω_{hop} [21]. Hence, for this class of organic semiconductors r is of the order of 10–1000, but the large variation even within this class shows that very different values can be expected for different organic semiconductors.

It is instructive to first consider a one-dimensional (1D) chain of sites for the case $E \gg \sigma/ea$, when all hops are down-field with the same rate ω_{hop}, leading to equal average waiting times $1/\omega_{hop}$ at each site. By solving the time-dependent Schrödinger equation for the spinor in the effective magnetic field and performing an average over the random hyperfine fields (in cylindrical coordinates ρ, ζ) [22], one can easily derive the following expression for the relative preservation, λ, of spin polarization, p, during the waiting time of the carrier at a site:

$$\lambda = \frac{1}{\sqrt{2\pi}} \int_0^\infty \rho d\rho \int_{-\infty}^\infty d\zeta e^{-(\rho^2+\zeta^2)/2} \frac{r^2+(\zeta+b)^2}{r^2+\rho^2+(\zeta+b)^2},$$
$$\approx \exp\{-[1/\ln(3)+r^2/2+b^2/2]^{-1}\}, \tag{1}$$

with $b \equiv B/B_{hf}$. This leads to an exponentially decaying polarization $p(x) = \exp(-x/l_s)$, with a spin-diffusion length $l_s = -a/\ln\lambda \approx a[1/\ln(3)+r^2/2+b^2/2]$. The increase of l_s with increasing b and r can readily be understood qualitatively: with increasing b, the Zeeman coupling becomes increasingly dominant over the hyperfine coupling and the carrier spin becomes effectively pinned. The quadratic increase with r results from "motional narrowing", well-known in magnetic-resonance spectroscopy.

For the three-dimensional (3D) situation we performed Monte Carlo simulations for hopping of a single carrier in a homogeneous electric field of arbitrary magnitude on a cubic lattice of sites ($N \times 50 \times 50$, where N is adapted to the specific situation), while *simultaneously* solving the time-dependent Schrödinger equation for its spinor [22]. The random site-energies and hyperfine fields are drawn from their corresponding Gaussian distributions. Sufficiently far from the injecting layer, $p(x)$ decreases exponentially, from which we extract l_s. We averaged over several thousands of energetic and hyperfine disorder configurations, making sure that the error bar in the plots discussed below is smaller than the symbol sizes shown.

In Fig. 1(b) we show l_s as a function of E for different reduced disorder strengths $\hat{\sigma} \equiv \sigma/k_B T$, for $r = 1000$ and $B = 0$. The arrow at the right axis shows the value obtained for the 1D model discussed above, which is quite close to the present results at large E. For other values of $r \gg 1$ (fast hopping) we find a similar dependence on E as shown in Fig. 1(b). For $r \lesssim 1$ (slow hopping) we find $l_s \sim a$, indicating that for this case no significant spin-diffusion length is found. The relevant case for the experiments carried out up to now [6–12] corresponds to $E \ll \sigma/ea$, so from now on we will focus on this case. We note that whereas l_s decreases steeply for $E \to 0$, it remains nonzero at $E = 0$.

The inset in Fig. 1(b) shows the carrier mobility μ as a function of E (for comparison: the unit μ_0 is of the order of $10^{-7} - 10^{-5}$ m^2/V s for the PPV derivatives studied in Ref. [21]). A strikingly different trend with increasing $\hat{\sigma}$ is observed for l_s compared to μ at small and intermediate E: while μ keeps on decreasing very rapidly with increasing $\hat{\sigma}$, l_s depends rather weakly on $\hat{\sigma}$ and even appears to saturate for large $\hat{\sigma}$. In order to provide an explanation for the weak dependence of l_s on $\hat{\sigma}$ we show in Fig. 2(a) the distribution $P(\tau)$ of waiting times τ [23] of the carrier while hopping through the lattice, at $E = 0$ and different $\hat{\sigma}$. The curves appear to saturate for large $\hat{\sigma}$. By considering hops upwards in energy from a Boltzmann distribution in the GDOS one can in fact prove [24] that $P(\tau)$ converges for large τ to a universal algebraic distribution $P(\tau) \sim \tau^{-3/2}$ in the limit $\hat{\sigma} \to \infty$, see the dashed line in Fig. 2(a). We note that $P(\tau)$ for a GDOS has been studied before [25], but for too small disorder strengths ($\hat{\sigma} \lesssim 4$) to observe this universal behavior.

The quite different dependencies of l_s and μ on $\hat{\sigma}$ can now be understood as follows. With increasing $\hat{\sigma}$ the tail of
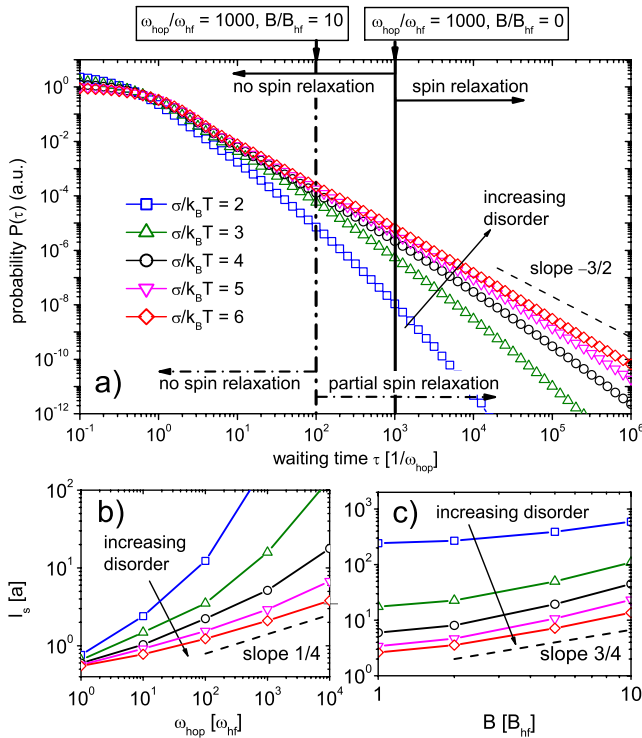
FIG. 2 (color online). (a) Waiting-time distributions (equally normalized) at $E = 0$ for different $\hat{\sigma} \equiv \sigma/k_B T$. Solid and dash-dotted lines and arrows: see the main text. (b) l_s at $E = 0.1\sigma/ea$ as a function of ω_{hop} at $B = 0$ and (c) as a function of magnetic field B for $r \equiv \omega_{hop}/\omega_{hf} = 1000$. The dashed lines in (a)–(c) indicate the expected power laws.

the distribution $P(\tau)$ contains an increasing amount of sites with very large τ, leading to a strong decrease of the mobility, since these sites cause a very long delay in the motion of the carrier. Regarding the spin diffusion, however, the situation is distinctly different. Let us, for example, consider the case $r = 1000$ and $B = 0$. At sites i with τ_i to the left of the solid line in Fig. 2(a), such that $r_i \equiv 1/\omega_{hf}\tau_i \gg 1$, essentially no polarization loss occurs [cf. Eq. (1) with r replaced by r_i]. At sites with τ_i to the right of this line, such that $r_i \ll 1$, almost immediate polarization loss occurs, but this effect is essentially the same for all these sites. For large $\hat{\sigma}$ the fraction of the latter sites, obtained by integrating $P(\tau)$ from the solid line to the right, converges to $\sim 1/r^{1/2}$. This means that on average the spin polarization disappears in $\sim r^{1/2}$ hops. Since at small E diffusion of carriers is dominant over drift one expects $l_s \sim (r^{1/2})^{1/2} \sim r^{1/4}$. The dashed line in Fig. 2(b) indicates this expected power law, to which the results indeed converge (for numerical reasons we took a small but finite E).

In Fig. 2(c) we plot l_s at small E as a function of magnetic field B, for $r = 1000$. For $B > B_{hf}$ we observe an important B-dependence, which again converges to a power law for increasing $\hat{\sigma}$. The analysis now goes as follows. Let us, for example, take $b = B/B_{hf} = 10$. From Eq. (1) (again replacing r by $r_i \equiv 1/\omega_{hf}\tau_i$) it follows

that if $r_i \gg b$, i.e., to the left of the dash-dotted line in Fig. 2(a), basically no polarization loss takes place. To the right of this line *partial* polarization loss takes place with $1 - \lambda \sim 1/b^2$, which is a consequence of the pinning effect of the Zeeman term discussed above. A similar argument as above now leads to the expectation $l_s \sim b^{3/4}$ in the diffusive regime, which is seen to be very well obeyed. Together with the above power-law dependence on r this allows us to estimate l_s for general values of $r \gg 1$ and b for the case of large $\hat{\sigma}$ and small E.

We now undertake a comparison between our theory and experimental results, as far as they are available at the moment. We have no information about the hopping frequencies of the OS used in the spin valves of Refs. [6–8]: sexithienyl, tris-(8-hydroxyquinoline) aluminum (Alq$_3$), and poly-3-hexylthiophene, respectively. Since the mobilities in these materials are higher than those of the PPV-derivatives investigated in Ref. [21], we expect that the hopping frequencies are such that $r > 1000$. A calculated value of $\sigma = 0.35$ eV for the energetic disorder of electrons in Alq$_3$ [26] leads to $\hat{\sigma} \approx 14$ at room temperature, which is clearly in the strong-disorder limit. We can conclude that with a typical value $a \approx 1$ nm the spin-diffusion lengths of about 10–100 nm found in Refs. [6–8] and recently confirmed with muon spin-resonance studies [10] are compatible with our results.

Very interestingly, inspection of the experimental GMR traces in Refs. [7,8], both using La$_{0.67}$Sr$_{0.33}$MnO$_3$ (LSMO) and Co as electrodes, reveals that in the up- and down-field sweeps the resistance as a function of B changes considerably already *before* the magnetization of the soft layer (with the weaker coercive field) is reversed. This points at a source of magnetoresistance other than the switching of the ferromagnetic layers and we propose that this is the magnetic-field dependence of the spin-diffusion length predicted by our theory. To illustrate its effect on the GMR traces, we simulated such traces using a simple phenomenological model. We describe the organic film by a reservoir for carriers with spin up and down, link the finite spin-diffusion length to the spin-flip rate between the two reservoirs, and derive an equation for the spin accumulation by solving the rate equations [22]. We fitted the resulting GMR traces to experimental data of Ref. [7]; see Fig. 3. The specific equation used in the fit reads: $MR(B) = MR_{max} \frac{1}{2}(1 + m_1(B)m_2(B)) \exp[-d/l_s(B)]$, with MR_{max} the MR when neglecting spin relaxation, d the thickness of the organic spacer, and we explicitly accounted for the fact that the system studied displays an opposite spin polarization for the parallel alignment of the magnetizations. The magnetization of electrode $i = 1, 2$ is represented by $m_i(B)$, measured along the applied field direction and normalized to the saturation magnetization. In this case we used an error function centered at the coercive field to match the rounded switching of the respective electrodes. For the B dependence of l_s we assumed $l_s(B) = l_{s,0}[\sqrt{1 + (B/B_0)^2}]^{3/4}$ with $B_0 = 2.3B_{hf}$,
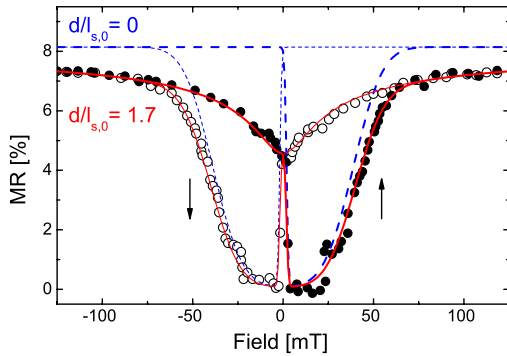
FIG. 3 (color online).   Full curves: fit of the model discussed in
the main text to the experimental magnetoresistance (MR) traces
taken from Fig. 3b of Ref. [7] (symbols). Dashed curves: results
neglecting spin relaxation. Thick/thin lines: up-/down-field
sweep.

as predicted by our theory in the diffusive regime ($E \ll
\sigma/ea$, see Fig. 2(c) and the fit in Ref. [22]). Figure 3 shows
that this predicted $l_s(B)$ accurately reproduces the shape of
MR(B) in the region before switching of the soft layer, with
a minimum number of parameters. The fitting procedure
yields $l_{s,0} \approx 1.7d$ and $B_{hf} \approx 5.7$ mT [22], the latter being
indeed a typical value for the random hyperfine field. The
simulated MR-trace for $d/l_{s,0} = 0$ (no spin relaxation)
deviates strongly from the experimental data, demonstrat-
ing that the latter cannot be explained assuming a
B-independent spin-diffusion length together with an in-
jected spin polarization proportional to the reported elec-
trode magnetization.

Our theory predicts a rather weak dependence of l_s on
the relative disorder strength σ/k_BT and hence on tem-
perature, in agreement with experiments [7,11,12]. In the
experiments with LSMO as one of the electrodes the GMR
effect decreases significantly above $T \approx 100$ K, but this
can be fully attributed to a reduction of the spin polariza-
tion of the injected current [11,12]. Finally, it is important
to note that in the experiments the GMR effect rapidly
disappears with growing bias voltage [7,11,12] on a volt-
age scale (~ 1 V) that corresponds in our theory to electric
fields for which $eEa/\sigma \ll 1$. At such fields, l_s has satu-
rated to its value at $E = 0$. Therefore, our view is that the
measured bias-voltage dependence is not caused by a
dependence of l_s on the electric field. Several possible
explanations for the steep decrease of spin-valve efficiency
with increasing bias have been suggested [11], but it is
clear that this issue requires much further study. If efficient
spin injection can be realized with high biases such that
$eEa/\sigma > 1$, our theory predicts greatly enhanced spin-
diffusion lengths of the order of several hundreds of nano-
meters, up to even millimeters [see Fig. 1(a)].

In summary, we have presented a theory for spin diffu-
sion in disordered organic semiconductors with hyperfine

coupling, based on a combination of incoherent carrier
hopping and coherent spin precession in a random effective
magnetic field. We obtain spin-diffusion lengths of the
correct magnitude that depend rather weakly on tempera-
ture, but considerably on the applied magnetic field, in
agreement with experiments on spin valves.

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