Hyperfine-induced spin relaxation of a diffusively moving carrier in low dimensions: implications for spin transport in organic semiconductors

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The hyperfine coupling between the spin of a charge carrier and the nuclear spin bath is a predominant channel for the carrier spin relaxation in many organic semiconductors. We theoretically investigate the hyperfine-induced spin relaxation of a carrier performing a random walk on a d-dimensional regular lattice, in a transport regime typical for organic semiconductors. We show that in $d = 1$ and $d = 2$ the time dependence of the space-integrated spin polarization $P(t)$, is dominated by a superexponential decay, crossing over to a stretched exponential tail at long times. The faster decay is attributed to multiple self-intersections (returns) of the random walk trajectories, which occur more often in lower dimensions. We also show, analytically and numerically, that the returns lead to sensitivity of $P(t)$ to external electric and magnetic fields, and this sensitivity strongly depends on dimensionality of the system ($d = 1$ vs. $d = 3$). Furthermore, we investigate in detail the coordinate dependence of the time-integrated spin polarization, $\sigma(r)$, which can be probed in the spin transport experiments with spin-polarized electrodes. We demonstrate that, while $\sigma(r)$ is essentially exponential, the effect of multiple self-intersections can be identified in transport measurements from the strong dependence of the spin decay length on the external magnetic and electric fields.

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I. INTRODUCTION

Spin dynamics of the charge carriers in organic semiconductors have attracted much attention recently. On one hand, the processes which underlie the use of these systems in the organic light-emitting diodes and organic photovoltaic solar cells, are explicitly spin-dependent, so that understanding of the spin dynamics in organic semiconductors is of fundamental interest for such applications. On the other hand, the long spin lifetimes of the carriers in the organic semiconductors make them an interesting candidate for prospective spintronic applications, and the detailed understanding of the mechanisms of the spin relaxation is required.

Typically, charge transport in organic semiconductors occurs via random (incoherent and inelastic) hopping of the polarons carrying positive or negative charge between localized molecular sites. During the waiting time between two consecutive hops the carrier spin interacts via hyperfine coupling with the spins of the nuclei (mostly, hydrogen), which surround the host site. Thus, the spin of the carrier waiting for the next hop undergoes rotation around a random axis by a random angle at each site. The principal role of this mechanism was experimentally confirmed and supported by a number of spin transport and spin resonance measurements, as well as theoretical works. Another source of spin relaxation is the spin-orbit interaction, which leads to the spin-flip scattering in the course of a hop, but this interaction in organic semiconductors is weak, so the hyperfine-induced spin relaxation is likely to be the main source of depolarization, although other theoretical and experimental studies favor the spin-orbit mechanism, and theoretical efforts are made to explain this controversy. Spin dynamics of the polarons in low-dimensional systems is of particular interest: in the polymer-based devices the carriers mostly move along the 1D polymer chains, while hopping from one polymer chain to another happens mostly at the intersections. One-dimensional organic polymer wires can be prepared and their properties can be studied in detail, see e.g. Refs. Also, engineering low-dimensional systems is a promising way to design organic materials with large magnetoresistance, which are of much technological interest.

This motivates the theoretical study, described below, of the hyperfine-induced spin relaxation of a carrier diffusing via random walk in $d = 1$ and $d = 2$ dimensions. We investigate in detail not only the (space-) integrated spin polarization $P(t)$ (which has been addressed in some previous works), but also the time-integrated polarization $\sigma(r)$ at the given point $r$ in space, which can be measured in spin-transport experiments. We show that for low-dimensional transport, these two quantities are related to each other in a rather non-trivial way. Moreover, we analyze the spin decay length $l_s$ for $d = 1$ and $d = 2$, and show that it is very sensitive to both electric and magnetic fields; this is important both for applications and for the fundamental studies of the transport in organic semiconductors.

The average polaron hopping rate $\nu$, corresponding to typical mobilities of $10^{-8}$ to $10^{-6}$ cm$^2$V$^{-1}$s$^{-1}$, is of the order of $1$–$100$ GHz. At the same time, the average hyperfine-induced spin precession frequency is of order $100$ MHz. Therefore, the hopping is much faster than the hyperfine precession, and the carrier performs many random-walk steps before its spin polarization averages out to zero. Thus, the spin relaxation should be sensitive to the statistics of the underlying random walk. The particularly important feature of the random walk is the...
the hyperfine fields. Also, it has been noticed that the\P{} to field.\end{equation}

FIG. 1: (Color online) Lateral (a) and vertical (b) spin valves
with organic active layer (gray), in which the charge carriers
are restricted to move in one-dimensional channels along
the x-direction. The separation between the injecting and
detecting electrodes is \( L \).

density of returns of the hopping carrier to the same
site, i.e. the frequency of the self-intersections of the
random walk trajectories. When the returns are absent, in
the so-called transient diffusion regime, the random
hyperfine field acting on the carrier’s spin has no memory:
the local hyperfine environments at different sites are un-
correlated, and the carrier hops from one site to another
never coming back. This corresponds to the motional
narrowing regime of the spin relaxation and leads to the
exponential decay of the space-integrated spin polarization,
\[ P(t) \propto \exp(-t/t_{S,1}) \], where \( t_{S,1} \) is the spin
relaxation time for the transient-diffusion regime. The
opposite scenario with frequent returns, known as the
persistent diffusion, takes place when the carriers move
in low-dimensional systems. The frequent returns to
the same site lead to the random hyperfine field with long
memory (long-time correlations), which suppresses the
motional narrowing and leads to faster spin relaxation.
The role of the memory of the hyperfine field has been
studied for some scenarios, and has been found to change
the spin relaxation of the spin polarization in \( d = 1 \) case
to \[ P(t) \propto \exp[-(t/t_{S,1})^{3/2}] \] at short times, with the
decay time \( t_{S,1} \) depending on the particular model for
the hyperfine fields. Also, it has been noticed that the
returns make \( P(t) \) very sensitive to the external magnetic
field.

However, the detailed knowledge about the carrier’s
spin relaxation in the case of low-dimensional transport is
still largely lacking, and our work aims at filling this gap.
We investigate analytically and numerically the spin
relaxation for lateral and vertical spin valves (Fig. 1),
with the carriers moving along the 1D current-carrying
channels. We consider the limit of small current density, when
each carrier moves independently of others, thus working
within the single-particle framework. For the lateral spin
valve, Fig. 1(a), the spin carrier hops along the very long
linear chain, performing an unbounded random walk.
For the vertical spin valve, Fig. 1(b), the random walk hap-

\begin{align*}
\text{pens over finite-size chain with reflecting boundaries. In}
\text{both cases we assume that the carrier is injected with the}
\text{spin state “up” at } x = 0, \text{ and its spin is probed by the}
\text{detector at } x = L.
\end{align*}

We study the space-integrated spin polarization \( P(t) \)
and the time-integrated polarization \( \sigma(r) \) at the given
point \( r \), which can be measured with the detector lead
at a given location. We demonstrate that these quanti-
ties exhibit remarkable universal features, and that the
returns in the course of the carrier diffusion play an im-
portant role in this relation.

First, for the time decay of \( P(t) \), we demonstrate the
evidence of the universal scaling: for different values of
the hyperfine coupling strength \( b_{hf} \) and hopping rate \( \nu \),
the decay of \( P(t) \) follows the same curve which depends
only on the normalized dimensionless time \( \tau = (\nu t)(b_{hf}/\nu)^{4/3} \).
This scaling holds not only for short times, where \( P(t) \) follows the previously known decay law
\[ P(t) = \exp[-(t/t_{S})^{3/2}] \], but also at long times, where we find a previously unnoticed stretched-exponential decay
\[ P(t) \propto \exp(-\alpha t^{3/4}) \] (for both spin valve geometries).
This scaling holds for both lateral and vertical spin-valve
geometries, at finite magnetic and electric field. Also,
we found that \( P(t) \), besides the known sensitivity to the
magnetic field, is also very sensitive to the electric field.
We have observed the similarly strong effect of the re-
turns for the spin relaxation in \( d = 2 \), leading to the
logarithmic corrections to the standard exponential de-
cay of \( P(t) \), and strong sensitivity to the external fields.

Second, we studied the time-integrated polarization
\( \sigma(r) \), which is of much importance for the spin-dependent
transport measurements. We are not aware of any analy-
tical theory for this quantity, but our numerical stud-
ies reveal unexpected universality in its behavior. For
persistent diffusion in low dimensions, in contrast to the
transient diffusion in 3D, the quantity \( \sigma(r) \) is not
directly related to \( P(t) \). Our numerical results show that,
beside the essentially non-exponential decay of \( P(t) \), the
spin transport decay is exponential, \( \sigma(r) \propto \exp(-r/l_{S}) \),
with high accuracy, even in the presence of the external
magnetic and electric fields. However, the resemblance
to the usual 3D transient-diffusion result is superficial:
for both \( d = 1 \) and \( d = 2 \) cases, the dependence of
the spin decay length \( l_{S} \) on the external fields is very strong,
in contrast to the standard 3D diffusion.

Our results suggest that the character of the carrier
diffusion in an organic semiconductor can be studied in
spin transport experiments, via the field dependence of
\( l_{S} \), and vice versa, the spin transport measurements
in low-dimensional organic semiconductors can be used for
accurate sensing of electric and magnetic fields, and for
other similar spintronic applications.

The rest of the paper is organized as follows. In the
next Section we discuss the formulation of the problem
and the methods used for analytical and numerical stud-
ies. In Sections III and IV we consider the spin relaxation
for the lateral and the vertical spin-valve geometries, re-
spectively. Section V outlines our results on the spin
relaxation in \(d = 2\). Details of the analytical calculations are presented in two Appendices.

II. MODEL FOR THE CARRIER SPIN RELAXATION

We consider a carrier hopping between sites, see Fig. 2(a), which model organic molecules or conjugated segments of polymers. Everywhere below, for both \(d = 1\) and \(d = 2\), we enumerate sites by the integer variable \(r\), so that e.g. for 1D chain the physical coordinate of the site is \(x = ar\), where \(a\) is the distance between the sites.

When the polaron is localized at the site with the radius-vector \(r\) its spin interacts with \(N\) nuclei \(I_{rk}\) \((k = 1, \ldots, N)\) surrounding the given site. Below we assume that all nuclei have spin 1/2, since the protons in many organic semiconductors are the most abundant species with the largest nuclear magnetic moment. The Hamiltonian governing the spin dynamics of the carrier localized at the site \(r\) is:

\[
H_r = BS_z + S \sum_{k=1}^{N} a_{rk} I_{rk}, \tag{1}
\]

where \(a_{rk}\) is the hyperfine coupling constant between the carrier spin and nuclear spin \(I_{rk}\), and \(B\) is the Larmor frequency of the carrier spin \(S\) in an external magnetic field along the \(z\) axis (everywhere below we take \(\hbar = 1\) and the electron’s gyromagnetic ratio \(\gamma_e = 1\), omitting the difference between the magnetic fields and the Larmor frequencies). Theoretical approach to the spin evolution in organic semiconductors customarily relies on the approximation where the quantum hyperfine field given by the sum in Eq. (1),

\[
\hat{b}_r = \sum_{k=1}^{N} a_{rk} I_{rk}, \tag{2}
\]

is approximated as a static classical vector \(b_r\) of random amplitude and direction, sampled from the Gaussian distribution with zero mean and the standard deviation equal to \(b_{hf} = \frac{1}{2} \sqrt{2 \chi \sum_k a_{rk}^2}\); this approximation is justified by the large number of nuclear spins coupled to the carrier spin at a given site \((N\) of order 10 or more\)). \(\beta\)

We also assume that the hyperfine fields at different sites are uncorrelated, so that \(\langle b_{\alpha r} b_{\beta r}^* \rangle_{hf} = b_{hf}^2 \delta_{\alpha \beta} \delta_{rr'}\), where \(\alpha, \beta = x, y, z\).

When we consider a carrier with the initial spin along \(\hat{z}\), performing a random walk with trajectory \(r(t)\), the carrier’s spin \(\mu(t)\) evolves according to the equation of motion

\[
\dot{\mu} = b_r(t) \times \mu(t) = \hat{\Omega}(r(t)) \mu(t), \tag{3}
\]

where the matrix

\[
\hat{\Omega}(r) = \begin{pmatrix}
0 & -b_r^x & b_r^y \\
-b_r^x & 0 & -b_r^z \\
b_r^y & b_r^z & 0
\end{pmatrix}, \tag{4}
\]

describes the spin rotation taking place at the site \(r\). Formal solution of this equation can be written in terms of the time-ordered exponent,

\[
\mu(t) = T \exp \int_0^t dt' \hat{\Omega}(r(t')) \mu(0),
\]

with the initial condition \(\mu(0) = \hat{z}\). The spin polarization is obtained by double averaging of the \(z\)-component of \(\mu(t)\),

\[
P(t) = \left\langle \langle \mu_z^2(t) \rangle \right\rangle \equiv \left\langle \left\langle T \exp \int_0^t dt' \hat{\Omega}(r(t')) \right\rangle \right\rangle_{hf} \langle \rangle_{rw} \langle \rangle_{zz}, \tag{5}
\]

where \(\langle \rangle_{rw}\) denotes averaging over the random walk trajectories, \(\langle \rangle_{hf}\) denotes averaging over the local hyperfine fields, and the indices \(zz\) denote that we need to take the \(zz\) entry of the matrix which results after the averaging of the time-ordered matrix exponent.

Without returns, all spin rotations at different sites would be independent and uncorrelated, leading to exponential decay of the polarization as a function of time (the motional narrowing regime). In the presence of the returns, the rotations at different moments of time are correlated, and the polarization decay accelerates. In \(d = 1\), the number of returns of the charge carrier to a given site after \(n\) hops is \(O(n^{1/2})\), whereas in \(d = 2\) and \(d = 3\) this number is \(O(\ln n)\) and \(O(1)\), respectively. Therefore one should expect that the influence of the returns is strong in \(d = 1\), modest in \(d = 2\), and weak in \(d = 3\) dimensions; below we concentrate mainly on the \(d = 1\) case where the effect is strongest.
The exact solution of Eq. (5) in the presence of returns is not available. In order to approach the problem, everywhere below we employ the fact that the hopping is much faster than rotation in the hyperfine field, so the parameter $\eta = b_{hf}/\nu$ is small. Indeed, the value of $b_{hf}$ is typically of order of 100 MHz, while the average carrier hopping rate $\nu$ is about 1–100 GHz, so

$$\eta = b_{hf}/\nu \sim 0.1 - 0.001 \ll 1.$$  

We can calculate $P(t)$ via the cumulant expansion in terms of the small parameter $\eta$:

$$P(t) = \left( T \exp\int_0^t dt' \hat{\Omega}(r(t')) \right)|_{\sigma=0} = \exp\left( \sum_n K_n(t) \right),$$

where $K_n(t)$ is proportional to $\eta^n$. The odd cumulants vanish (since the local Gaussian distributions of $b_r$ have zero mean), the first non-vanishing cumulant $K_2(t)$ will determine the behavior of $P(t)$, at least at short times. We will demonstrate the accuracy of this approach by comparing the analytically calculated $K_2(t)$ with the results of the direct numerical simulations.

The numerical simulations are even more important for studying the time-integrated polarization $\sigma(r)$. We are not aware of any analytical theory for this quantity which would provide insights and guide our investigation. Thus, we rely solely on the numerical results, which demonstrate surprising and interesting universal features of $\sigma(r)$.

One could do numerical simulations by Monte-Carlo sampling of the random-walk trajectories and the distributions of the local fields, thus calculating the average in Eq. (5) directly. However, our results show that the statistical error is quite large, so instead we employ the approach based on the Liouville equation.

We describe the carrier spin via its density matrix $\rho_r(t) = \frac{1}{2} \{ q_r(t) + m_r(t) \sigma \}$, where $q_r(t)$ is the probability to find the carrier at site $r$ at time $t$, and $m_r(t)$ is its spin polarization; $\sigma$ is the vector of Pauli matrices. The carrier dynamics obeys the master equation

$$\frac{d\rho_r}{dt} = \sum_{r'} [W_{r',r} q_{r'}(t) - W_{r,r'} q_r(t)], \quad (6)$$

where $W_{r,r'}$ is the hopping rate from site $r$ to $r'$. At the same time, the spin polarization follows the generalized drift-diffusion equation

$$\frac{dm_r}{dt} = \sum_{r'} [W_{r',r} m_{r'}(t) - W_{r,r'} m_r(t)] + b_r \times m_r. \quad (7)$$

For the charge carrier initially injected at the site $r = 0$ in the spin-up state, the initial conditions correspond to $q_0(0) = \delta_{r,0}$ and $m_0(0) = \delta_{r,0} \sigma$ with $\sigma(0) = (0, 0, 1)$ (directed along the $z$-axis). The solution $m_r(t)$ of Eq. (7) includes averaging over the random-walk trajectories of the duration $t$, but the hyperfine fields at each site are taken as having some specific directions and amplitudes, i.e. the set $\{b_r\}$ of the local fields is fixed. Averaging over the local hyperfine fields is performed via Monte-Carlo sampling of $\{b_r\}$ at each site from the Gaussian distribution $\mathcal{N}(b_r) = (2\pi b_{hf})^{-3/2} \exp(-b_r^2/2b_{hf}^2)$.

In particular, in this way we determine the time-integrated spin polarization at a given location,

$$\sigma(r) = \nu \int_0^\infty dt \langle m_z^2(t) \rangle_{hf},$$

which plays an important role in the spin transport measurements.

The effect of the external magnetic field is included into our model by simply adding the external field $B$ to the local hyperfine fields. The external electric field $E$ applied along the $x$-axis (Figs. 1 and 2) is taken into account by modifying the hopping rates: the hops along the field are more probable than backwards. Below, we assume, in the spirit of the Miller-Abrahams theory, that the backward hopping rate $\nu_b$ (upwards in the electric field potential) is exponentially suppressed in comparison with the forward hopping rate $\nu_f$ (downwards in the electric potential), i.e. $\nu_b = (\nu_f/2) \exp(-\varepsilon)$, where $\varepsilon = eEa/k_BT$ with the Boltzmann constant $k_B$ and temperature $T$, and $eEa$ is the electric potential difference between two neighboring sites, while the forward–hopping rate remains unchanged, $\nu_f = \nu/2$. In particular, for $d = 1$, we have

$$W_{r,r'} = (\nu/2) \delta_{r,r' - 1} + (\nu/2) \delta_{r,r' + 1} \quad \text{for } E = 0, \quad (8)$$

$$W_{r,r'} = (\nu/2) \delta_{r,r' - 1} + (\nu e^{-\varepsilon}/2) \delta_{r,r' + 1} \quad \text{for } E \neq 0.$$

### III. SPIN RELAXATION IN A LATERAL SPIN VALVE

We neglect the effect of injector/detector electrodes, assuming insignificant tunneling between the leads and the semiconductor. For the lateral spin valve this implies unbounded diffusion over an infinite chain. For numerical simulations, we used a long chain with periodic or reflecting boundary conditions; the length was large enough to ensure vanishing population near the ends at all times. We also excluded from consideration the additional spin relaxation which is possible at the interface between a ferromagnetic electrode and an organic active layer.

#### A. $P(t)$ and $\sigma(r)$ in the absence of external fields

Important insights about the short-time behavior of $P(t)$ can be obtained analytically, using the lowest orders of the cumulant expansion in terms of the small parameter $\eta = b_{hf}/\nu$,

$$P(t) = \exp \left( \sum_n K_n(t) \right) \approx \exp \left[ K_2(t) \right].$$
Our calculations in Appendix B show that it has small

The next non-vanishing cumulant, \( K_4 \), is determined by the 4-th order correlation function of the process \( \hat{\Omega}(r(t_2)) \). Our calculations in Appendix B show that it has small numerical prefactor, \( K_4(t) \approx 0.01 \cdot \eta^4(\nu t)^3 \), so that this cumulant becomes comparable to \( K_2 \) only at rather long times. Thus, \( K_2(t) \) dominates the polarization decay at small times:

\[
P(t) \approx e^{K_2(t)} = e^{-t/(\nu t_S)^{3/2}}, \quad t_S = \frac{3 \sqrt{2 \pi}}{8 \eta^2} \cdot \frac{2}{\nu}.
\]

Excellent accuracy of this scaling at short times is seen from comparison with the direct numerical simulations in Fig. 3. The similar decay law, \( P(t) \sim \exp(-t^{3/2}) \), has been obtained in earlier studies, which assumed the single-axis local hyperfine fields (directed along the \( z \)-axis)\(^{24-26} \), or the hyperfine fields with fixed amplitude randomly distributed in the \( x-y \) plane\(^{18} \). Our results confirm this decay law for the hyperfine fields distributed isotropically in space, and show that this feature holds for a very wide range of problems related to the spin decay during 1D diffusion; we will also see the same decay law below, for the vertical spin valve case.

More importantly, we notice that \( K_2(t) \) and \( K_4(t) \) depend only on the single dimensionless renormalized time \( \tau = (\nu t)^{1/3} \). From Eqs. (7) and (8) one can see that all cumulants, as well as \( P(t) \) itself, are functions of two dimensionless quantities, \( \nu t \) and \( \eta \). However, our analytical and numerical studies evidence a much stronger result, that \( P(t) \) is a function of a single dimensionless quantity \( \tau \). We performed a series of simulations for different values of \( \eta \), and Fig. 3 shows that all results fall on the same universal curve \( F(\tau) \), given in the inset of Fig. 3. This holds at all times we studied, even at large \( \tau \), when the contribution from the high-order cumulants is important.

Even more, we see that the same scaling holds when we consider the polarization decay at finite magnetic fields, finite electric fields, as well as for the case of the vertical spin valve (both without fields and with external magnetic and/or electric fields). Thus, it is highly likely that the renormalized time \( \tau \) represents a universal feature of the spin decay for \( d = 1 \) random walk. Understanding of this remarkable scaling, as far as we know, is lacking.

Another interesting feature, seen from Fig. 3 is the decay of \( P(t) \) at long times, which has a stretched-exponential form \( P(t) \sim \exp(-\alpha \eta t^{3/4}) \), with \( \alpha = 1.33 \); we checked that this form remains very accurate all the way down to \( P(t) \sim 10^{-12} \). Again, to our knowledge, the reasons for this behavior are not understood yet.

Equally interesting is the behavior of the time-integrated polarization \( \sigma(r) \). We are not aware of any analytical theory, which would provide insights in the behavior of this quantity and guide our simulations. Thus, we rely solely on the numerical results.

Our numerical simulations show that in the whole range of parameters \( \sigma(r) \) has the exponential form, \( \sigma(r) = l_S \exp(-|r|/l_S) \). Without external fields, the time-integrated polarization precisely follows the scaling law \( \sigma(r) = \eta^{-2/3} G(r\eta^{1/3}) \), where the scaling function \( G(w) = 0.68 \exp(-1.47|w|) \) is obtained from numerical fitting. The origin of this scaling, as well as the origin of the exponential dependence of \( \sigma(r) \), are not clear.

Note that the exponential decay of \( \sigma(r) \) in the case of 1D persistent diffusion is not trivial. If multiple returns were negligible (as in transient diffusion in 3D), \( P(t) \) would decay exponentially with the decay time \( l_{st}^{-1} \); the space- and time-integrated polarizations then would be related by the simple convolution\(^{40} \), \( \sigma(r) = \nu \int_0^\infty dt P(t) q_r(t) \), where \( q_r(t) \) is the probability to find the carrier at the site \( r \) at time \( t \), see Eq. (9). This would lead to the exponential decay \( \sigma(r) = \exp(-|r|/l_{st}) \), with the well-known diffusion relation \( l_{st} = \sqrt{D t_{st}} \), where \( D \) is the diffusion coefficient (for a random walk on a \( d \)-dimensional lattice, \( D = \nu a^2/2d \), where \( a \) is the average distance between the sites).

However, in our case, where the returns are crucial, \( \sigma(r) \) and \( P(t) \) are not related in such a simple way, and it is not even clear whether such a relation exists. Indeed, if
we used the same convolution of the non-exponential \( P(t) \) with \( q_{\tau}(t) \) for 1D diffusion, we would obtain clearly non-exponential decay law for \( \sigma(r) \). Thus, the origin of the exponential decay for \( d = 1 \) must be different from that of \( d = 3 \) case; this guess is supported by the qualitative difference in response of \( P(t) \) and \( \sigma(r) \) to the external magnetic and electric fields between the \( d = 1 \) and \( d = 3 \) cases.

\section*{B. Role of external magnetic field}

It has been noticed previously\(^\text{18} \) that in low dimensional diffusion, in the presence of multiple returns, \( P(t) \) is very sensitive to the external magnetic field. For the magnetic field \( \mathbf{B} \), the cumulant expansion of \( P(t) \) can be carried out after applying the rotating-frame transformation, \( \mathbf{\mu}(t) \rightarrow \exp(t\mathbf{\Omega}_B)\mathbf{\mu}(t) \), where \( \mathbf{\Omega}_B \) is the skew-symmetric matrix formed of \( \mathbf{B} \) (see Appendix A). Taking the external field as directed along the \( z \)-axis, we find the second cumulant

\[
K^B_2(t) = -2b_{hf}^2 \int_0^t dt_1 \int_0^{t_1} dt_2 \cos \left( B(t_1 - t_2) \right) \frac{\cos \left( B(t_1 - t_2) \right)}{2\pi\nu(t_1 - t_2)}.
\]  

(11)

It is instructive to compare Eqs. (11) and (9): the cosine term in the integrand is the only difference between the cumulants \( K^B_2 \) for zero magnetic field and \( K^B_2 \) for finite magnetic field. This term induces a cutoff for \( t \gtrsim B^{-1} \), reducing the integral significantly. This is somewhat similar to motional narrowing: because of the external magnetic field, the transversal components of the total field seen by \( \mathbf{\mu} \) average out on the timescale \( B^{-1} \).

Comparing Eqs. (10) and (11), one can see that the cutoff induced by the external magnetic field becomes important for \( B \sim t_S^{-1} \sim \eta^{-1/3}b_{hf} \), which is even smaller than \( b_{hf} \). Our numerical results (Fig. 4(c)) clearly verify this sensitivity already at very low fields. This behavior is in striking contrast with the transient diffusion in 3D, where the spin relaxation time would scale as \( t_{S,1r} \propto (1 + (B/\nu)^2) \), meaning that the magnetic field effects would be visible only at very large fields \( B \sim \nu \gg b_{hf} \).

The time-integrated spin polarization \( \sigma(r) \) also exhibits strong sensitivity to the external magnetic field. It still has exponential form, \( \sigma(r) \propto \exp \left[ -|r|/l_S(B) \right] \), but the spin decay length sensitively depends on \( B \); Fig. 4(b) illustrates this dependence for \( \eta = 0.01 \). The magnetic field dependence of the (normalized) spin decay length, \( l_S(B)/l_S(0) \), is plotted in Fig. 4(c). Again, the analogy to the case of the transient 3D diffusion is superficial; this point is demonstrated in more detail in Appendix A (see Eq. (A13)), where the transient diffusion case is analyzed, and its qualitative difference with our results for \( d = 1 \) are emphasized.

\section*{C. Role of external electric field}

If a drive voltage is applied to the spin valve (Fig. 1), the resulting electric field \( \mathbf{E} = E\hat{x} \) leads to a change in the hopping rates along and against the field direction (forward and backward hopping rates \( \nu_f \) and \( \nu_b \), see Fig. 2(b)). Utilizing the Miller-Abrahams hopping model\(^\text{20} \) we take \( \nu_b = (\nu/2)\exp(-e) \), where \( e = eEa/k_BT \), and \( \nu_f = \nu/2 \) (independent of \( E \)). Overall, this would lead to slower motion of the carrier, implying slower changes of the random hyperfine field acting on it, and therefore (as it happens in the motional narrowing scenario) would produce faster decay of \( P(t) \) with increasing \( e \). In the regime of 3D transient diffusion (see Appendix A for details) this is the most important effect: \( P(t) \) would decay exponentially, and the decay time would decrease as \( (\nu_f + \nu_b)/\nu \).

However, in the persistent-diffusion regime, the returns are important; besides inducing faster hopping, the electric field also changes the statistics of the returns. By making the forward hops more probable, the probability of the returns is decreased, thus profoundly affecting the carrier spin relaxation. As above, we calculate the short-time behavior of \( P(t) \) using the cumulant expansion, and the second cumulant in the presence of finite electric field is

\[
K^E_2(t) = -b_{hf}^2 \int_0^t dt_1 \int_0^{t_1} dt_2 \frac{e^{-\sqrt{\nu_f\nu_b}|t_1-t_2|}}{\sqrt{\pi}(t_1-t_2)}.
\]  

(12)
changes with electric field.

IV. SPIN RELAXATION IN A VERTICAL SPIN VALVE

The geometry of the vertical spin valve, Fig. 1(b), suggests diffusion over a linear chain of finite length \( L \). Neglecting the back-tunneling into the electrodes, as it often happens in experiments, we obtain the perfectly reflecting boundaries. The spin relaxation now depends on the length of the system: \( P(t) = P(t, L) \), \( \sigma(r) = \sigma(r, L) \). Another feature of this geometry is that, instead of the whole function \( \sigma(r, L) \), one is interested in its value at the detection electrode, \( \sigma_s(L) \equiv \sigma(L, L) \).

A. \( P(t) \) and \( \sigma_s(L) \) in the absence of external fields

Let a carrier be implanted at the boundary site, \( r = 1 \), of a linear chain of finite length \( L \). After \( n \) hops it will diffusively cover the distance \( \sim \sqrt{n} \). With the hopping rate \( \nu \) one has \( n \approx \nu t \), so that for relatively short times, \( \nu t < L^2 \), the boundary at \( r = L \) will not affect the spin relaxation noticeably. Therefore, for relatively short times, \( P(t) \) can be found by considering a carrier diffusing over the semi-infinite chain, \( r = 1, 2, \ldots \), with the reflecting boundary at \( r = 1 \). Calculation carried out in Appendix B for this case gives the second cumulant function,

\[
K_2^G(t) \approx -\frac{8\nu^2}{3\sqrt{\pi}}(\nu t)^{3/2},
\]

which differs from \( K_2 \) of the infinite chain, Eq. (9), only by the factor \( \sqrt{2} \). The ensuing short-time superexponential dependence of \( P(t) \) is confirmed in our simulations, see Fig. 4.

At longer times, the influence of both boundaries becomes noticeable, and the decay of the spin polarization will depend on \( L \). This dependence can be guessed using the results for unbounded diffusion given above.

As we have seen in the previous Section, the characteristic length of the spin relaxation is \( l_s \), and scales with \( \eta \equiv b_{dL}/\nu \) as \( \eta^{-2/3} \). Based on this fact and on Eq. (13), we can guess that the spin polarization should depend on the dimensionless time \( \tau = (\nu t)\eta^{-1/3} \) and on the dimensionless length \( \lambda = l_s\eta^{-1/3} \). Our numerical simulations confirm the expected scaling law \( P(t, L) = F(\tau, \lambda) \), and provide the most notable features of the scaling function \( F(\tau, \lambda) \). In Fig. 6(a)–(c), we demonstrate the scaling by plotting \( P(t, L) \) as a function of \( \tau \) and \( \lambda \), for three different values of \( \lambda \) and twelve different values of \( \eta \).

These figures also show that the scaling function has the superexponential form \( F(\tau, \lambda) \equiv \exp\left(-8\tau^{3/2}/3\sqrt{\pi}\right) \) at small times \( \tau \lesssim 0.5 \), in accordance with Eq. (13), and is independent of the normalized chain length \( \lambda \). At large times, the scaling function is accurately described by the stretched exponential, \( F(\tau, \lambda) \equiv \exp\left(-\alpha(\lambda)\tau^{\beta(\lambda)}\right) \), with

\[
\alpha(\lambda) \equiv 1.5, \quad \beta(\lambda) \equiv 0.85,
\]
Our simulations (Fig. 7) show that it remains essentially exponential, with the parameters which depend on the chain length; specifically, $\beta(0.75) = 0.59$, $\beta(1.25) = 0.61$, and $\beta(2) = 0.64$ in Figs. 6(a)-(c), respectively. As the length of the chain increases, the exponent $\beta$ increases, saturating at the value $\beta = 0.75$ for very large $\lambda$ that corresponds to the unbounded diffusion [see Fig. 6(d)].

In a similar way, we numerically verify the existence of scaling for the time-integrated spin polarization. As we expect, all length scales are divided by the factor $\eta^{-2/3}$, so that $\sigma(t, L) = \eta^{-2/3}G(\eta^{-2/3} L \mu^{-2/3})$, in analogy with the case of unbounded diffusion in the lateral spin valve. Correspondingly, for the spin polarization $\sigma_\epsilon(L)$, observed at the detector electrode, we have the scaling $\sigma_\epsilon(L) = \eta^{-2/3} G_\epsilon(\eta^{-2/3} L \mu^{-2/3})$. The numerical fitting shows that the scaling function is very accurately described as exponential, $G_\epsilon(w) = 2.712 \exp(-1.475 w)$. This corresponds to the dependence, $\sigma_\epsilon(L) = 4L^{-\lambda} \ln(\frac{L}{L_S})$, with the diffusion length, $L_S = 0.678 \eta^{-2/3}$, which is nearly identical to the one found for the unbounded diffusion in the lateral spin valve.

### B. Role of external magnetic and electric fields

In analogy with the case of the lateral spin valve, we studied the influence of the magnetic field $B \hat{z}$ along the $z$-axis, and of the electric field $E \hat{x}$ directed along the $x$-axis, on the spin relaxation.

We are primarily interested in the behavior of $\sigma_\epsilon(L)$. Our simulations (Fig. 6) show that it remains essentially exponential with $L$, in both external magnetic and electric fields. Thus, the field dependence of $\sigma_\epsilon(L)$ is fully encompassed by the field dependence of the spin decay length on $B$ and $\epsilon = 25\gamma T/\kappa B T$, shown in Figs. 7(b) and (d). As before, we see that the returns lead to strong sensitivity of $L_S$ to the external fields, and this dependence is very close to its analog established in the previous Section. The curves in Figs. 7(b) and (d) appear to resemble the ones in Fig. 7(c) and Fig. 7(c).

### V. SPIN RELAXATION IN $d = 2$

Above we focused on the analysis of the spin relaxation of a diffusing carrier for $d = 1$, mainly because the effect of multiple returns is strongest in this case. Meanwhile, it is rather straightforward to extend our analysis to the $d = 2$ case. For a carrier performing a simple random walk over a regular lattice in $d = 2$, the second cumulant function is calculated in Appendix B. It suggests the short-time decay

$$P(t) \simeq \exp[-2 \eta^2 (vt) \ln(\gamma vt)/\pi],$$

where $\gamma = 5.243$ is a numerical coefficient. We have checked numerically that this formula accurately describes the spin relaxation down to rather small polarization values. Specifically, at $P(t) \sim 0.05$, the observed deviation from Eq. (14) was only about 0.002. Our simulations have also shown that at longer times the decay slows down, closely resembling exponential. This is shown in Fig. 8(a), which illustrates the spin relaxation...
in a system with $\eta = 0.025$. Thus, in $d = 2$ the effect of multiple returns is quite noticeable. Meanwhile, it is rather easy to check that in $d = 3$ the polarization decay is exponential at virtually all times.

To understand the spin-transport relaxation in $d = 2$, we consider a lateral spin valve device similar to that of Fig. 1(a), where the carriers hop between the sites of $d = 2$ regular lattice located in the $x$-$z$ plane [see Fig. 2(c)], so that each site is characterized by the radius vector $\mathbf{r} = (x, z)$, with $x, z = 0, \pm 1, \pm 2, \ldots$. Assuming that the size of the organic layer in the $z$-direction is much larger than the spin diffusion length, we characterize the spin-transport relaxation by the quantity,

$$\sigma_{2d}(x) = \sum_{x=L}^{x=-L} \sigma(x, z) \equiv \nu \sum_{x=L}^{x=-L} \int_0^\infty dt \langle \mathbf{m}_x^2(t) \rangle_{\text{hf}}, \quad (15)$$

which is the total time-integrated spin polarization that has reached the detection electrode at $x = L$. Here $\mathbf{m}_x(t)$ is the solution of drift–diffusion equation (7) for the 2D regular lattice; we solve this equation numerically, with the initial condition $\mathbf{m}_x(0) = \hat{x}_0 \sigma(0) \mathbf{m}(0)$. The influence of the external magnetic and electric fields is taken into account as described above.

Our results show that the decay of $\sigma_{2d}(x)$ is exponential, both with and without the external fields. The spin diffusion length $l_S$ is also rather sensitive to the external fields, as a result of the returns in the course of the 2D random walk. This is illustrated in Figs. 5(b) and (c), where we compare the results for the random walk in different dimensions for $\eta = 0.025$, where the spin diffusion length in the absence of the external fields is $l_S = 9.0$. From the results of Section III one can see that the same zero-field spin diffusion length in $d = 1$ corresponds to $\eta_1 \approx 0.021$, whereas for $d = 3$, from the strong collision approximation (i.e., by neglecting multiple returns) we find the same zero-field spin diffusion length for $\eta_3 \approx 0.032$ [cf. Eq. (A13)]. Therefore, in Figs. 8(b) and (c) we compare the field dependence of the normalized spin diffusion length, $l_S(B)/l_S$ and $l_S(E)/l_S$, for a diffusion in $d = 1$ with $\eta_1 = 0.021$ (orange), $d = 2$ with $\eta = 0.025$ (black), and $d = 3$ with $\eta_3 = 0.032$ in strong-collision approximation (dashed line).

VI. CONCLUSION

We have investigated spin relaxation of a carrier performing a random walk on a lattice, with random magnetic fields at each site. This models spin relaxation in organic semiconductors, where the charge transport between the $\pi$-conjugated segments of molecules is incoherent, and where the carrier spin interacts with the hydrogen nuclear spins surrounding a segment. Due to relatively large number of surrounding nuclear spins and their slow dynamics, the on-site random magnetic fields are taken as static, and sampled from the Gaussian distribution. The width of the distribution reflects the strength of hyperfine coupling at each site. For the incoherent hopping we assumed a random walk with the constant transition rates.

To understand the effect of multiple self-intersections of random walks, we have focused on the motion in $d = 1$ dimensional infinite linear chain. A superexponential short-time decay of spin polarization, $P(t) \sim \exp(-\alpha t^{3/2})$, was found analytically from the cumulant expansion. The numerical simulations confirmed the superexponential dependence, and showed that it changes to a stretched exponential at longer times. We have also analyzed the spin relaxation of a carrier diffusing over a linear chain of finite length, and established that the short-time relaxation is somewhat faster, $P(t) \sim \exp(-\sqrt{2} \alpha t^{3/2})$, whereas the stretched exponential long-time decay becomes slower. As a consequence of the multiple returns, in all these cases $P(t)$ is highly sensitive to the external magnetic and electric fields. For a diffusion over $d = 2$ regular lattice, we have found the short-time behavior $P(t) \sim \exp(-\alpha_2 t^{3/2})$, smoothly crossing over to the exponential long-time decay.

Due to its relevance for the spin transport experiments, we have investigated the spin relaxation in the space domain, considering the time-integrated spin polarization $\sigma(\mathbf{r})$. It was demonstrated that, despite the strongly non-exponential decay in time, the spin relaxation in space is essentially exponential, superficially similar to that of a carrier diffusing in $d = 3$. However, diffusion in lower di-
mensions shows much stronger sensitivity to the external electric and magnetic fields.

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Appendix A

In this Appendix we calculate spin relaxation for a carrier diffusing transiently, i.e., when self-intersections of its random-walk trajectories are negligible, and the strong-collision approximation is valid. Our starting point is Eq. (5) of the main text. Let $r(t)$ be a random walk trajectory that starts at $r_0 = 0$ and passes through $n$ sites, $r_1, ..., r_n$. Then the time-ordered exponent can be written as

$$ T \exp \int_0^t dt' \Omega (r(t')) = e^{\tau \Omega (r_n)} \cdots e^{\tau \Omega (r_0)} , \quad (A1) $$

where $\tau_k$ are the waiting time at $r_k$, $k = 0, 1, ..., n$. In the absence of self-intersections all $\tau_k$ are different, and the average of Eq. (A1) over the local hyperfine frequencies is a product of exponentials, averaged over the independent Gaussian distributions of hyperfine frequencies $\{b_{r_k}\}$, namely

$$ \langle T \exp \int_0^t dt' \Omega (r(t')) \rangle_{b_{r_k}} = \prod_{k=0}^n e^{\tau_k} . \quad (A2) $$

where $f(\tau)$ is defined by $\langle e^{\tau \Omega (b)} \rangle_{\{b\}} = \hat{1} f(\tau)$, with $\Omega _b$ being the skew-symmetric matrix formed of $b$. By averaging

$$ e^{\tau \Omega (b)} = \hat{1} + \sin(b|\tau|) \frac{\Omega (b)}{|b|} + 2 \sin^2(b|\tau/2|) \frac{\Omega ^2 (b)}{|b|^2} , \quad (A3) $$

over the Gaussian distribution of $b$ with zero mean and standard deviation, $b_{\text{std}}$, one gets:

$$ f(\tau) = \frac{1}{3} + \frac{2}{3} (1 - b_{\text{std}}^2 \tau^2) \exp(-b_{\text{std}}^2 \tau^2/2) . \quad (A4) $$

When a longitudinal magnetic field $B = B \hat{z}$ is applied, Eq. (A3) should be averaged over a Gaussian distribution of $b$ with the mean, $\langle b \rangle = B \hat{z}$. Even though this leads to a non-diagonal matrix $\langle e^{\tau \Omega (b)} \rangle_{\{b\}}$, it remains block-diagonal, so that Eq. (A2) holds with a modified $f(\tau)$. Note in passing that $f(\tau)$ is a typical example of the static Kubo-Toyabe relaxation function.\textsuperscript{41,42}

Next we want to average Eq. (A2) over the waiting time distributions and random-walk trajectories. Because of the absence of returns, the latter reduces to a summation over all $n$, whereas the former can be done by integrating $f(\tau)$ with the waiting-time distribution function, $\nu e^{-\nu \tau}$. Hence from Eqs. (A3) and (A2) we get:

$$ P(t) = \sum_{n=0}^\infty \int_0^\infty dt_0 \cdots \int_0^\infty dt_n \prod_{j=0}^n f(\tau_j) \nu e^{-\nu \tau} \times \left[ \theta \left( t - \sum_{k=0}^{n-1} \tau_k \right) - \theta \left( t - \sum_{k=0}^n \tau_k \right) \right] . \quad (A5) $$

Here, the difference of $\theta$-functions guarantees that at time $t$ the walker has performed exactly $n$ steps, so that $\sum_{k=0}^{n-1} \tau_k < t < \sum_{k=0}^n \tau_k$. Using the integral representation, $\theta(x) = \int [e^{iz \tau}/(z - i \epsilon)] dz/(2\pi i)$, we reduce Eq. (A5) to

$$ P(t) = \int_{-\infty}^{\infty} \frac{dz}{2\pi i} e^{izt} u(1) - u(1 + iz) , \quad (A6) $$

where $u(y) = \nu \int_0^\infty d\tau f(\tau)e^{\nu \tau}$. Going back to the definition of $f(\tau)$ and taking the $\tau$-integral we get:

$$ u(y) = \frac{1}{y} \int d^3 \xi \frac{|\xi|^2}{(2\pi)^3} \left( \frac{|y\eta|^2 + (\zeta_z + \beta)^2}{|\xi|^2 + \zeta_z^2 + \zeta_y^2 + (\zeta + \beta)^2} \right) , \quad (A7) $$

which in fact provides a good approximation for any $\beta$. Form Eq. (A7) we find $z_0 \approx 2i/|\eta|^2 + \beta^2 + 1$, yielding

$$ P(t) \approx e^{-t/z_0} , \quad t_0 = (|\eta|^2 + \beta^2 + 1)/2\nu . \quad (A9) $$

The spacial dependence of spin polarization is given by

$$ \sigma (\mathbf{r}) = \nu \int dt \sum_{n=0}^\infty Q_n (\mathbf{r}) \int_{0}^{\infty} dt_0 \cdots \int_{0}^{\infty} dt_n \prod_{j=0}^n f(\tau_j) \nu e^{-\nu \tau_j} \times \left[ \theta \left( t - \sum_{k=0}^{n-1} \tau_k \right) - \theta \left( t - \sum_{k=0}^n \tau_k \right) \right] , \quad (A10) $$

where $Q_n (\mathbf{r})$ is the probability that the random walker is at $\mathbf{r}$ after $n$ steps. Calculating the integrals in Eq. (A10) is easy by taking first the $t$-integral. Further, introducing $\bar{u} = \nu^2 \int d\tau f(\tau)e^{-\nu \tau}$ and using Eq. (A8), we find:

$$ \sigma (\mathbf{r}) = \bar{u} \sum_{n=0}^\infty Q_n (\mathbf{r}) \left[ u(1) \right] ^n \approx \sum_{n=0}^\infty Q_n (\mathbf{r}) e^{-n/\nu t_0} . \quad (A11) $$
The probability $Q_{\omega}(r)$ is related to the solution of Eq. (6) as $q_{\omega}(t) = e^{-\nu t} \sum_{n=0}^{\infty} Q_{\omega}(r) (\nu t)^n / n!$. This can be used in Eq. (A11) to express $\sigma(r)$ in terms of $q_{\omega}(t)$:

$$\sigma(r) \simeq \nu \int_0^\infty dt q_{\omega}(t) P(t). \quad (A12)$$

The large-$r$ behavior of $\sigma(r)$ follows from that of $q_{\omega}(t)$. Namely, for a simple random walk on a $d$-dimensional regular lattice one has $q_{\omega}(t) = (2\pi \nu/d)^{-d/2} \exp[-d|\mathbf{r}|^2/(2\nu t)]$, leading to the exponential decay, $\sigma(r) \propto \exp(-|\mathbf{r}|/l_S)$, with

$$l_S(B) = \sqrt{\frac{\nu^2 \Omega(B)}{2d}} \simeq \frac{1}{4d\eta} \sqrt{1 + (\eta B/b\eta t)^2}. \quad (A13)$$

In an external electric field, $\mathbf{E} = E\mathbf{x}$, hopping rates along $\mathbf{x}$ are changed. This leads to the drift along $\mathbf{x}$, and also modifies the diffusion and the waiting-time distribution. While $P(t)$ is affected only because of the change in waiting-time distribution, $q_{\omega}(t)$ and consequently $\sigma(r)$ are sensitive to the drift and diffusion. Assuming a random walk over a $d$-dimensional regular lattice, and for the hopping model considered in the main text, the hopping rates forward and backward to $\mathbf{x}$ are $\nu_f = \nu/2d$ and $\nu_b = \nu e^{-\varepsilon}/2d$, where $\varepsilon = eEa/k_B T$, whereas in perpendicular directions hopping rates are $\nu/2d$. From the corresponding waiting-time distribution function, $\nu e^{-\nu t}$ with $\nu = \nu_f + \nu_b + (d-1)/d$, one finds $P(t) \simeq \exp[-t/t_S^2(\varepsilon)]$ with the electric-field dependent spin relaxation time,

$$t_S^2(\varepsilon) = \frac{1}{2\nu \eta^2} \left( \frac{2d - 1 + e^{-\varepsilon}}{2d} \right) + \frac{\beta^2 + 1}{\nu} \frac{d}{2d - 1 + e^{-\varepsilon}}. \quad (A14)$$

The drift-diffusion equation (6) in $d = 3$ dimensions has the solution,

$$q_{\omega}(t) = \left( \frac{\nu_f}{\nu_b} \right)^\frac{\beta}{2} e^{-\nu t} I_x(2\sqrt{\nu \eta t}) I_y(\nu t/d) I_z(\nu t/d), \quad (A15)$$

where $\mathbf{r} = (x, y, z)$ with $x, y, z = 0, \pm 1, \pm 2, \ldots$ and $I_\alpha$ is the modified Bessel function of order $\alpha$. For a spin valve similar to those illustrated in Fig. 1 we evaluate the quantity, $\sigma(x) = \sum y, z \sigma(r)$ (in lower dimensions, one or both of last terms in Eq. (A13) should be eliminated, and the sum for $\sigma(x)$ should be changed correspondingly). After taking this sum, the integral Eq. (A12) reduced to the Laplace transform for a modified Bessel function, yielding $\sigma(x) \propto \exp[-x/l_S(\varepsilon)]$ for all $x > 0$, where

$$l_S(\varepsilon) = \frac{1}{\ln \left( \frac{1}{2} (1 + e^{-\varepsilon}) + \frac{d}{\nu^2 \Omega(B)} + \sqrt{\frac{1}{2} (1 + e^{-\varepsilon}) + \frac{d}{\nu^2 \Omega(B)}}^2 - e^{-\varepsilon} \right)}. \quad (A16)$$

This dependence is plotted in Fig. 5(c) for a system with $\beta = 0$ and $l_S(0) = 14.9$ (corresponding to $\eta = 0.0336$ in $d = 1$), and in Fig. 8(c) for a system with $\beta = 0$ and $l_S(0) = 9$ (corresponding to $\eta = 0.0322$ in $d = 3$).

**Appendix B**

In this Appendix we calculate the $d = 1$ dimensional second cumulant functions, $K_2$, $K_2^B$, $K_2^P$, $K_2^E$, $K_2^\omega$, Eqs. 9, 11, 12, and 13, the fourth cumulant function $K_4$, as well as the second cumulant for a simple random walk on a two-dimensional regular lattice, $K_2^{(2)}$. Basic ingredients of this calculation are the Markov property of random walk and its Greens function, $G(\mathbf{r}, \mathbf{r'}, t)$, which is the solution of corresponding random walk equation (6) with the initial condition, $q_{\omega}(0) = \delta_{\mathbf{r}, \mathbf{r'}}$. The second cumulant function of Eq. (5) is defined by

$$K_2(t) = \int_0^t dt_1 \int_0^{t_1} dt_2 \langle \Omega(t_1) \Omega(t_2) \rangle_{zz}, \quad \langle \Omega(t_1) \Omega(t_2) \rangle \equiv \langle \Omega(\mathbf{r}(t_1)) \Omega(\mathbf{r}(t_2)) \rangle_{hit}^{tw}, \quad (B1)$$

where the average over random walk trajectories and locally Gaussian hyperfine frequencies is meant. Using the matrix form, Eq. (11), and the fact that the components of $b_r$ are delta-correlated, $\langle b^o \cdot b^o_{r'} \rangle_{hit} = -b^2_{hit} \delta_{r, r'} \delta_{\alpha, \beta}$, one easily takes the average over local frequencies, resulting in $\langle \Omega(t_1) \Omega(t_2) \rangle = -\mathbf{l} \cdot 2 b^2_{hit} \langle \delta_{r(t_1), r(t_2)} \rangle_{tw}$. For any type of random walk, this can be expressed via the Greens function as follows:

$$\langle \Omega(t_1) \Omega(t_2) \rangle = -\hat{\mathbf{l}} \cdot 2 b^2_{hit} \sum \mathbf{r} G(\mathbf{r}, \mathbf{r}, t_1 - t_2) G(0, \mathbf{r}, t_2). \quad (B2)$$
For the random walk on an infinite chain we have $G(r, r', t) = e^{-\nu t} I_{\nu - r} (\nu t)$, where $I_r(z)$ is the modified Bessel function of order $r$. From Eq. (B2) we find, \( \langle \langle \Omega(t_1) \Omega(t_2) \rangle \rangle_{zz} = -2 b_{\text{hf}}^2 e^{\nu t(t_1 - t_2)} I_0(\nu(t_1 - t_2)) \), which gives the second cumulant,
\[
K_2(t) = -2 \eta^2 \int_0^{\nu t} dz_1 \int_0^{z_1} dz_2 e^{-(z_1 - z_2)} I_0(z_1 - z_2).
\] (B3)

In view of large $\eta$, it is necessary to find the integral for large $(\nu t) \gg 1$. Utilizing the large-$z$ asymptote $e^{-z} I_r(z) \simeq (2\pi z)^{-1/2} e^{-z^2/2}$ in the integrand, we arrive at the result Eq. (B3).

As the odd cumulants are zero, the fourth cumulant function is expressed in terms of the four-time correlation function as follows:
\[
\frac{1}{2} K_4^2(t) + K_4(t) = \int_0^{t_1} dt_1 \int_0^{t_2} dt_2 \int_0^{t_3} dt_3 \int_0^{t_4} \langle \langle \Omega(t_1) \Omega(t_2) \Omega(t_3) \Omega(t_4) \rangle \rangle_{zz}.
\] (B4)

From Eq. (1) we find that the $zz$-component of the product $\Omega(t_1) \Omega(t_2) \Omega(t_3) \Omega(t_4)$ is equal to
\[
b_{r(t_2)}^2 \left[ b_{r(t_1)}^2 b_{r(t_4)}^2 + b_{r(t_1)} b_{r(t_2)} b_{r(t_3)} b_{r(t_4)} \right] + \left[ b_{r(t_1)} b_{r(t_2)} b_{r(t_3)} + b_{r(t_1)} b_{r(t_2)} b_{r(t_3)} + b_{r(t_1)} b_{r(t_2)} b_{r(t_3)} \right] \left[ b_{r(t_3)} b_{r(t_4)} + b_{r(t_3)} b_{r(t_4)} \right].
\] (B5)

To find $\langle \langle \Omega(t_1) \Omega(t_2) \Omega(t_3) \Omega(t_4) \rangle \rangle_{zz}$, we first average Eq. (B5) over the local hyperfine field distribution, then over the random walk trajectories. After the first averaging we get:
\[
\langle \langle \Omega(t_1) \Omega(t_2) \Omega(t_3) \Omega(t_4) \rangle \rangle_{zz} = b_{\text{hf}}^4 \left[ \delta(t_1, t_2) \delta(t_3, t_4) + 2 \delta(t_1, t_3) \delta(t_2, t_4) + 4 \delta(t_1, t_4) \delta(t_2, t_3) \right] \langle \langle \Omega(t_1) \Omega(t_2) \rangle \rangle_{rw}.
\] (B6)

This equation follows from the calculation of local field averages of the form, $\langle b_{r(t_1)} b_{r(t_2)} b_{r(t_3)} b_{r(t_4)} \rangle_{bf}$. For $\alpha \neq \beta$, this calculation is simple and gives $b_{\text{hf}}^4 \delta_{r_1, r_2} \delta_{r_3, r_4}$. For $\alpha = \beta$, on the other hand, it results in the combination, $b_{\text{hf}}^4 \left( \delta_{r_1, r_2} \delta_{r_3, r_4} + \delta_{r_1, r_3} \delta_{r_2, r_4} + \delta_{r_1, r_4} \delta_{r_2, r_3} \right)$. Note that contributions with $r_1 = r_2 = r_3 = r_4$ cancel out from this combination due to the Gaussian character of local frequency distributions.

Next we average Eq. (B6) over the random walk trajectories. For a function of four coordinates, $f$, and times arranged as $t_1 \geq t_2 \geq t_3 \geq t_4$, from the Markov property of random walk one generally has:
\[
\langle \langle f(r(t_1), r(t_2), r(t_3), r(t_4)) \rangle \rangle_{rw} \approx \sum_{r_1, r_2, r_3, r_4} f(r_1, r_2, r_3, r_4) G(r_1, t_1) G(r_2, t_2) G(r_3, t_3) G(r_4, t_4),
\] (B7)

where $r_{ij} = r_i - r_j$ and $t_{ij} = t_i - t_j$. We apply Eq. (B7) with the infinite-chain Greens function to each term of Eq. (B6), and find the large-$\nu t$ asymptotes of the resulting quantities:
\[
\langle \langle \delta_{r_1, r_2} \delta_{r_3, r_4} \rangle \rangle_{rw} = G(0, t_{12}) G(0, t_{34}) \approx \frac{1}{2\pi \nu \sqrt{t_{12} t_{34}}},
\] (B8)
\[
\langle \langle \delta_{r_1, r_2} \delta_{r_3, r_4} \rangle \rangle_{rw} = \sum_r G(r, t_{12}) G(r, t_{23}) G(r, t_{34}) \approx \frac{1}{2\pi \nu \sqrt{t_{13} t_{24} - t_{23}^2}},
\] (B9)
\[
\langle \langle \delta_{r_1, r_2} \delta_{r_3, r_4} \rangle \rangle_{rw} = G(0, t_{23}) \sum_r G(r, t_{12}) G(r, t_{34}) \approx \frac{1}{2\pi \nu \sqrt{t_{14} t_{23} - t_{23}^2}}.
\] (B10)

Equations (B6) and (B8)-(B10) define the integrand of Eq. (B4). Using the asymptotic forms, we find:
\[
\int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \int_0^{t_3} dt_4 \langle \langle \Omega(t_1) \Omega(t_2) \Omega(t_3) \Omega(t_4) \rangle \rangle_{zz} \approx \frac{5}{9} \eta^4(\nu t)^3.
\] (B11)

This relation, together with Eq. (B4), leads to the result,
\[
K_4(t) \simeq \left[ (5\pi - 16)/9\pi \right] \eta^4(\nu t)^3.
\] (B12)
entail a factorization of four-time functions, as it happens in Eq. (B15), whereas Eqs. (B19) and (B20) do not satisfy this condition.

Consider now the spin polarization decay in $d = 1$, in the presence of a magnetic field along $\hat{z}$. This case can be described by adding in Eq. (7) the term $B \times m_r$, where $B = B\hat{z}$. A straightforward evaluation of $\langle \langle \Omega(t_1) \Omega(t_2) \rangle \rangle$ by repeating the steps that have led from Eq. (11) to Eq. (13) is insufficient; magnetic field effects appear only in the fourth order, as a correction to $K_4$ of order $\sim (Bb)^2$. Rather, a systematic expansion of $P(t)$ in powers of $B^2$ can be achieved after performing the rotating-frame transformation, $m_r(t) = \exp(t \Omega_B) m_r(0)$. Then $m_r(t)$ satisfies Eq. (7) with time-dependent local frequencies, $\tilde{\nu} = \nu - B \cdot \tilde{\nu}$, and initial condition, $m_r(0) = \delta_\nu m(0)$. Also, as $\exp(t \Omega_B)$ does not change the $z$-component of the vector on which it acts, $P(t)$ is expressed through $m_r(t)$ exactly in the way it was in terms of $m_r(t)$. Averaging over the distribution of local hyperfine fields now gives $\langle \langle b(t_1) b(t_2) \rangle \rangle \sim -2 b^2 \delta_{\nu} \cos(B|t_1 - t_2|) \tilde{\nu}(t_1, t_2)$, which leads to Eq. (11) after applying Eq. (22) and large-$\nu t$ expansion of the resulting Bessel function.

$$K_2^E(t) = -2 b^2 \int_0^t \int_0^{t_1} e^{-(\nu f + \nu_0)[t_1 - t_2]} I_0(2\sqrt{\nu f \nu_0}(t_1 - t_2)) \simeq -\frac{b^2}{(\nu f \nu_0)^{1/4}} \int_0^t \int_0^{t_1} e^{-(\sqrt{\nu f - \nu_0})^2(t_1 - t_2)} \sqrt{\pi(t_1 - t_2)}. \quad (B13)$$

The $E$-dependence of $K_2^E(t)$ is non-trivial because the prefactor in Eq. (B13) grows as $\exp(\varepsilon/4)$, while the integral is suppressed with $E$. To clarify this dependence and to show that, for almost all $t$, the absolute value of the cumulant decreases with increasing $E$, we plot $\exp[K_2^E(t)]$ with $\eta = 0.05$ in Fig. 9 for three different values of $E$.

To find the cumulant function $K_2^E(t)$ for the case of a random walk over the semi-infinite chain, $r = 1, 2, \ldots$, with the reflecting boundary at $r = 1$, we exploit its Greens function, $G(r, r', t) = e^{-\nu t} [I_{r-r'}(\nu t) + I_{r+r-1}(\nu t)]$. Plugging this Greens function in Eq. (11) and using the large-$\nu t$ expansion of the modified Bessel function yields

$$\langle \langle \Omega(t_1) \Omega(t_2) \rangle \rangle \simeq -\sqrt{\frac{2}{\varepsilon}} \left( \frac{1}{\sqrt{t_2 - t_1}} + \frac{1}{\sqrt{t_1 + t_2}} \right). \quad (B14)$$

By further integration we find the cumulant function Eq. (13).

The regular lattice in $d = 2$ can be described by the radius-vector, $r = (x, y)$, with $x, y = 0, \pm 1, \pm 2, \ldots$, and $\hat{x}, \hat{y}$ along the lattice sides. The Greens function of the random walk over this lattice is $G^{(2)}(r, r', t) = e^{-\nu t} I_{|x-x'|}(\nu t) I_{|y-y'|}(\nu t)$. Further extension of Eqs. (B11)-(B13) to $d = 2$ is straightforward, leading to

$$K_2^{(2)}(t) = -2 b^2 \int_0^t \int_0^{t_1} e^{-(\nu f + \nu_0)t_2} I_0(\nu(t_1 - t_2)/2) = -2 \eta^2 \int_0^t \frac{\nu t}{e^{-\varepsilon t} I_0(z/2)}. \quad (B15)$$

Combining numerical integration and asymptotic expansion of $I_0(z)$ for large $z$, we find the large-$z$ expansion,

$$\int_0^z \frac{\nu t}{e^{-\varepsilon t} I_0(z/2)} = \frac{1}{\pi} \ln(\gamma z) - \frac{1}{2\pi} \ln(z) + \zeta + O(1/z), \quad \gamma \approx 5.243, \quad \zeta \approx -0.264, \quad (B16)$$

yielding

$$K_2^{(2)}(t) \simeq -2 \eta^2(\nu t) \ln(\gamma \nu t)/\pi. \quad (B17)$$

![FIG. 9: (Color online) $\exp[K_2^E(t)]$ is plotted against $\nu t$ from Eq. (B13) with $\eta = 0.05$, for $\varepsilon = 0$ (red), $\varepsilon = 0.5$ (green), and $\varepsilon = 1$ (blue). Open black circles are simulated points for $P(t)$ with corresponding values of parameters.](image-url)
