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Quantum dynamics of nuclear spins and spin relaxation in organic semiconductorsV. V. Mkhitarian¹ and V. V. Dobrovitski^{1,2}¹*Ames Laboratory, Iowa State University, Ames, Iowa 50011, USA*²*QuTech and Kavli Institute of Nanoscience, TU Delft, Lorentzweg 1, 2628 CJ Delft, Netherlands*

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We investigate the role of the nuclear-spin quantum dynamics in hyperfine-induced spin relaxation of hopping carriers in organic semiconductors. The fast-hopping regime, when the carrier spin does not rotate much between subsequent hops, is typical for organic semiconductors possessing long spin coherence times. We consider this regime and focus on a carrier random-walk diffusion in one dimension, where the effect of the nuclear-spin dynamics is expected to be the strongest. Exact numerical simulations of spin systems with up to 25 nuclear spins are performed using the Suzuki-Trotter decomposition of the evolution operator. Larger nuclear-spin systems are modeled utilizing the spin-coherent state P -representation approach developed earlier. We find that the nuclear-spin dynamics strongly influences the carrier spin relaxation at long times. If the random walk is restricted to a small area, it leads to the quenching of carrier spin polarization at a nonzero value at long times. If the random walk is unrestricted, the carrier spin polarization acquires a long-time tail, decaying as $1/\sqrt{t}$. Based on the numerical results, we devise a simple formula describing the effect quantitatively.

DOI: [10.1103/PhysRevB.95.214204](https://doi.org/10.1103/PhysRevB.95.214204)**I. INTRODUCTION**

One of the most remarkable characteristics of organic semiconductors is long spin coherence times, which makes these materials suitable for various applications in spintronics [1–3] and magnetotransport devices [4–12]. The reason behind this valuable property is that the light elements, such as hydrogen and carbon, from which organic semiconductors are composed, have very weak spin-orbit interaction, so that the relaxation of the carrier spin induced by the spin-orbit coupling [13–16] is diminished. As a result, the hyperfine coupling between the charge carrier and hydrogen nuclear spins can be the main source of the carrier spin scattering [7–9,17–19] and the resulting spin relaxation.

Due to the inherently present disorder, charge transport in organic semiconductors occurs via incoherent diffusive random walk over the charge-carrying molecules or π -conjugated segments of polymers. During the waiting time between two consecutive hops the carrier spin and the local hydrogen nuclear spins couple via a hyperfine interaction. Existing theories of hyperfine-induced spin relaxation and more general spin-dependent phenomena in organic semiconductors approximate the hyperfine interaction by locally random static magnetic fields, acting on the carrier spin [15,16,20–25]. This provides a semiclassical approximation to the quantum spin dynamics. The distribution of random magnetic fields is taken to be Gaussian. The hyperfine interaction strength is then controlled by the mean-square deviation of the Gaussian distribution b_{hf} . Experimentally established values of b_{hf} are of the order of a few milliteslas.

The semiclassical approximation neglects the action of the carrier spin on the local nuclear-spin environment. Thus it is good for relatively slow nuclear-spin dynamics and fast carrier hopping. However, the semiclassical approximation may be inadequate if the carrier spends a long time at the molecular sites, leading to sizeable changes in the local spin environments. This can happen, e.g., if the carrier moves in effectively low dimensions, so that it visits the same site many times. In this case the average time spent on a given site

depends primarily on the probability of multiple returns to the same site. For a one-dimensional diffusive random walk of a total duration t , the average time spent by a carrier on a given site on its trajectory is $\sim\sqrt{t\tau_0}$, and in $d = 2$ dimensions this time is $\sim\tau_0 \ln(t/\tau_0)$, where τ_0 is the average waiting time, i.e., the average time between consecutive hops [26]. In both these cases the time spent by the carrier at one site can become sufficiently long for the quantum dynamics of the local spin environment to be important. This is unlike the random walk in $d = 3$, where the time spent on a site is $\sim\tau_0$ and is independent of t due to the vanishing probability of returns [26].

In this paper we investigate the effect of nuclear-spin quantum dynamics on the spin relaxation in $d = 1$. We utilize numerical simulations based on a Monte Carlo sampling of random-walk trajectories. To simulate the spin dynamics of small systems with up to 25 total nuclear spins we employ the Suzuki-Trotter decomposition of the evolution operator [27,28]. For systems with a larger number of nuclear spins we make use of the coherent-state P -representation approach for quantum central-spin dynamics [29,30].

We study the time decay of the average spin polarization of a carrier spin $P(t)$ initially injected into an organic layer in the spin-up state [$P(0) = 1$]. The spin polarization evolves as the carrier walks randomly over a linear chain of L molecular sites, and its spin interacts with N nuclear spins at each site. The decay of $P(t)$ is controlled by the dimensionless combination $\eta = (b_{\text{hf}}\tau_0)$ [21,24,25], which is the average precession angle of carrier spin between two consecutive hops (we take $\hbar = 1$ and the electron gyromagnetic ratio, $\gamma_e = 1$, making the magnetic fields and the Larmor frequencies equivalent). We focus on small $\eta \ll 1$, characteristic of organic semiconductors featuring long spin coherence time.

Our calculations prove that the initial, dominant decay of spin polarization, down to about $P(t) = 0.05$, is insensitive to the dynamics of nuclear spins and can be obtained accurately from the semiclassical approximation. Therefore the results of previous studies based on the semiclassical approach [24,25] remain valid for the initial decay of $P(t)$.

The effect of quantum dynamics of nuclear spins develops at longer times. For relatively small L and N , we observe a plateau-like long-time behavior of $P(t)$, where its value is about $(LN)^{-1}$, independent of η . This is in sharp contrast to the semiclassical behavior. For finite N and $L \rightarrow \infty$ we find yet another unique long-time dependence, namely, $P(t) \approx \alpha(N\sqrt{t/\tau_0})^{-1}$, where $\alpha \approx 0.43$. On the other hand, for finite L and increasing N , the long-time polarization disappears, and $P(t)$ simply regains the semiclassical form.

This paper is organized as follows. In the next section we discuss the hyperfine interaction between the carrier and hydrogen nuclear spins and its semiclassical description in terms of random static magnetic fields. Our results on the spin relaxation by a quantum nuclear-spin bath and a comparison with those of the semiclassical approximation are presented in Sec. III. We discuss our results and provide explanations for the common features and differences of the quantum and semiclassical results in Sec. IV.

II. THE HYPERFINE INTERACTION AND ITS SEMICLASSICAL DESCRIPTION

We consider a diffusive random walk of a carrier over a linear chain of L molecular sites. Accordingly, the sites are enumerated by the scalar coordinate, $r = 1, \dots, L$. At each molecular site r , the carrier spin $\mathbf{S} = 1/2$ couples to $k = 1, 2, \dots, N$ nuclear spins $\mathbf{I}_{r,k} = 1/2$ by a hyperfine interaction. We will consider an isotropic hyperfine coupling, governed by the Hamiltonian

$$H_r = B_0 S_z + \mathbf{S} \sum_{k=1}^N a_k \mathbf{I}_{r,k}, \quad (1)$$

where B_0 is the external magnetic field along the z axis and $\{a_k\}_{k=1}^N$ are the hyperfine coupling constants. This description implies that the carrier-host molecular sites are identical, so that a_k do not depend on r .

Quite generally, theories of spin-related phenomena in organic semiconductors approximate the quantum Overhauser field, given by the sum in Eq. (1), by a constant classical vector,

$$\mathbf{b}_r = \sum_{k=1}^N a_k \mathbf{I}_{r,k}, \quad (2)$$

which is not affected by the interaction [20]. The approximation (2) can be justified as follows. With the interaction (1), the nuclear-spin precession period scales as \sqrt{N} [31]. Therefore, for large N one can neglect the slow dynamics and consider the nuclear spins to be static. For large N it is also reasonable to approximate the distribution of \mathbf{b}_r by the Gaussian with the standard deviation, $b_{\text{hf}} = \frac{1}{2} \sqrt{\sum_k a_k^2}$.

While one expects that the approximation (2) is good for increasingly large N , its accuracy for finite N in the presence of hopping needs to be critically investigated. In organic materials $N \approx 10$ is the expected number of hydrogen nuclei coupled to a carrier spin at a molecular site [9,21]. With such a moderate value of N , the relaxation of a diffusing carrier spin can still be sensitive to the quantum dynamics of nuclear spins.

III. CALCULATION OF SPIN RELAXATION CAUSED BY A QUANTUM NUCLEAR-SPIN BATH

In this section we calculate the spin relaxation of a carrier performing a diffusive random walk over a linear chain of L sites. At each site the carrier spin couples to N nuclear spins according to the Hamiltonian (1). We assume that the random hops occur between the nearest-neighbor sites with equal probability. Accordingly, the random waiting times have the average, τ_0 , which is uniform for all sites, and the waiting time distribution at each site is Poissonian, $\mathcal{N}(\tau) = \tau_0^{-1} \exp(-\tau/\tau_0)$. Note that by this choice of $\mathcal{N}(\tau)$ we neglect the energy and positional disorder of molecular states, which would lead to a spread in local values of τ_0 . For finite L , the boundary conditions for the random walk should also be specified. However, simulations with periodic and reflective boundaries yield very close results, so that below we present the results only for the periodic boundary conditions.

Our calculation of the spin relaxation is based on the following simple consideration. A carrier, initially injected at $r = r_0$ in the spin-up state $|\uparrow\rangle$, diffusively moves over the available molecular sites and suffers spin flips. The system thus begins its evolution from the initial spin state, $|\psi(0)\rangle = |\uparrow\rangle \otimes |\chi\rangle$, where $|\chi\rangle$ is the initial wave function of all LN nuclear spins. In the course of the carrier random walk with the trajectory $r(t)$, the spin state of the system evolves according to the Schrödinger equation, $i\partial_t |\psi(t)\rangle = H_{r(t)} |\psi(t)\rangle$. Its solution can be formally written in terms of the time-ordered exponent [32],

$$|\psi(t, [r(t)])\rangle = T \exp\left(-i \int_0^t dt' H_{r(t')}\right) |\uparrow\rangle \otimes |\chi\rangle. \quad (3)$$

By writing $[r(t)]$ in the argument we emphasize that $|\psi(t, [r(t)])\rangle$ is the spin wave vector after time t , provided that the carrier underwent a random walk with the trajectory $r(t)$. The carrier spin polarization can be defined as $P(t) = 2\overline{S_z(t)}$, with the bar standing for a triple average, where the first is the quantum-mechanical average, the second is the average over the possible quantum states of the nuclear-spin bath, and the third extends over different realizations of random-walk trajectories. Thus

$$P(t) = 2\langle\langle\langle\psi(t, [r(t)])|S_z|\psi(t, [r(t)])\rangle\rangle\rangle_{\{\chi\}}_{\text{rw}}. \quad (4)$$

The calculation of $P(t)$ from Eq. (4) can be carried out numerically by utilizing the Suzuki-Trotter decomposition [27–29] of the time-ordered exponent in Eq. (3), combined with a Monte Carlo sampling of random-walk trajectories. However, the computer memory requirements impose limitations on the number of spins that can be modeled [29] because the required memory grows exponentially with the number of modeled spins. In our case this means that the total number of nuclear spins, LN , is restricted to 20–30.

Based on the above scheme, we have simulated the quantum spin dynamics of various systems with up to 25 nuclear spins, uniformly distributed over $L = 3 - 25$ molecular sites. Representative results of such simulations for a system of $L = 5$ sites and $N = 4$ spins per site with $\eta \equiv (b_{\text{hf}}\tau_0) = 0.1$ and a system of $L = 7$ sites and $N = 3$ spins per site with $\eta = 0.167$ are demonstrated in Figs. 1(a) and 1(b), respectively. The plots also contain semiclassical results for the same

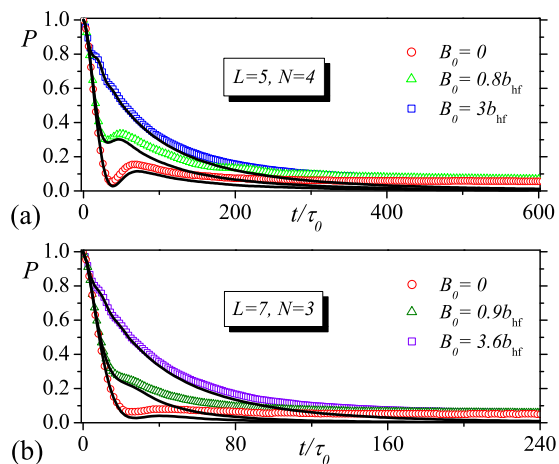


FIG. 1. Spin relaxation in various applied magnetic fields, obtained with the numerically exact simulation of quantum spin dynamics. The numerical results for $P(t)$ are plotted with open symbols, while the black lines are the results of the semiclassical approximation. (a) System of $L = 5$ and $N = 4$ nuclear spins per site, with $\eta \equiv (b_{\text{hf}}\tau_0) = 0.1$ and the hyperfine couplings $a_1 = 0.83b_{\text{hf}}$, $a_2 = 0.9b_{\text{hf}}$, $a_3 = 1.05b_{\text{hf}}$, and $a_4 = 1.18b_{\text{hf}}$. Plotted are the results for relaxation in the applied fields $B_0 = 0$ (red), $B_0 = 0.8b_{\text{hf}}$ (green), and $B_0 = 3b_{\text{hf}}$ (blue). (b) System of $L = 7$ sites and $N = 3$ nuclear spins per site, with $\eta = 0.167$ and $a_1 = 1.3b_{\text{hf}}$, $a_2 = 1.15b_{\text{hf}}$, and $a_3 = 0.99b_{\text{hf}}$. Red, dark green, and violet symbols represent the applied fields $B_0 = 0$, $B_0 = 0.9b_{\text{hf}}$, and $B_0 = 3.6b_{\text{hf}}$, respectively.

systems, obtained from the semiclassical approximation (2) (for details of the semiclassical calculation of spin relaxation see Ref. [25]). At small t , the quantum and semiclassical results in Fig. 1 coincide. This indicates that the initial decay of $P(t)$ is not very sensitive to the quantum dynamics of nuclear spins. On the other hand, there is a large qualitative discrepancy between the quantum and semiclassical results at longer times. Thus the long-time behavior of $P(t)$ is not captured by the semiclassical approximation; while the latter predicts a vanishing spin polarization, the decay of $P(t)$ shows a long-time plateau behavior, quenching at a small but finite value.

The quenching of $P(t)$ at long times, seen in Fig. 1, is a consequence of the nuclear-spin dynamics. However, further analysis of the effect of nuclear-spin dynamics requires a modeling of larger spin systems. To this end we employ the P -representation method for quantum spin system simulation [29,30]. The method is based on a Monte Carlo sampling of the density matrix in the spin coherent-state basis, allowing an efficient modeling of large quantum systems with thousands of bath spins. It also allows assessment of the spin dynamics at considerably longer times.

To check the accuracy of the P -representation method for the problem at hand, we compare its outcome for systems of up to 25 nuclear spins with the results of exact simulation. The comparison verifies the efficiency and accuracy of the P -representation approach to our problem. We demonstrate typical examples of such a comparison in Fig. 2 by plotting the quantum simulation results of Fig. 1 together with the P -representation curves for the same systems. The P -representation curves in Fig. 2 virtually coincide with the exact

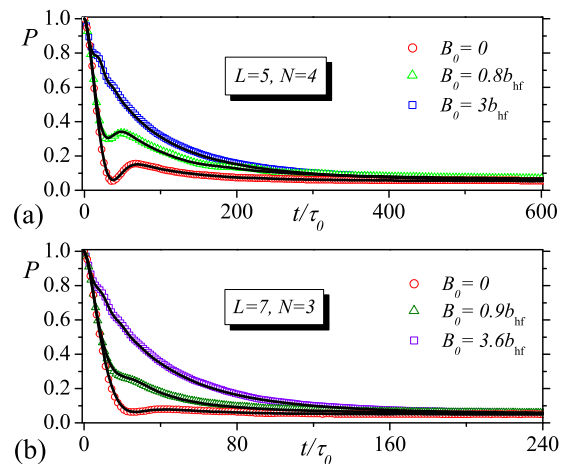


FIG. 2. Numerically exact calculation results from Fig. 1 (open symbols) are plotted together with the results obtained from the P -representation simulations (black lines). The comparison confirms the high accuracy of the P -representation approach to this problem.

simulation results in both short- and long-time domains, and only a minor deviation can be observed at the intermediate times.

With the P -representation method at hand we are able to investigate both larger spin systems and longer times. In particular, we examine the long-time behavior of the spin relaxation in the regime $\eta \ll 1$ (corresponding to fast hopping), where the relaxation is slow.

Our P -representation simulations reinforce the previous conclusion that at long times the decay of $P(t)$ is very slow, so that the spin polarization nearly quenches to a few percent of its original value. We also find that the value of $P(t)$ at the long-time plateau is almost insensitive to η . This is shown in Fig. 3, where $P(t)$ is plotted for various values of η for the system with $L = 5$, $N = 4$. Moreover, as seen in Figs. 1 and 2, the plateau value of $P(t)$ is almost independent of the external magnetic fields of the order of b_{hf} . Therefore the plateau value is universal in the sense that it is determined by L and N and is practically independent of η and B_0 .

Further numerical analysis of the long-time dynamics shows that the amplitude of the long-time plateau of $P(t)$ decreases with both L and N . Specifically, for not too large L and N the amplitude of the long-time plateau scales as $(LN)^{-1}$. For $\eta = 0.1$, we demonstrate this dependence in

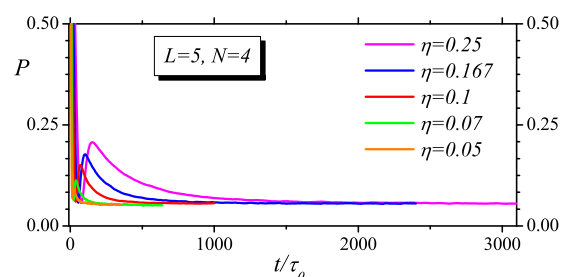


FIG. 3. Long-time behavior of $P(t)$ for $L = 5$, $N = 4$, and $\eta = 0.25$ (orange), $\eta = 0.167$ (green), $\eta = 0.1$ (red), $\eta = 0.07$ (blue), and $\eta = 0.05$ (magenta).

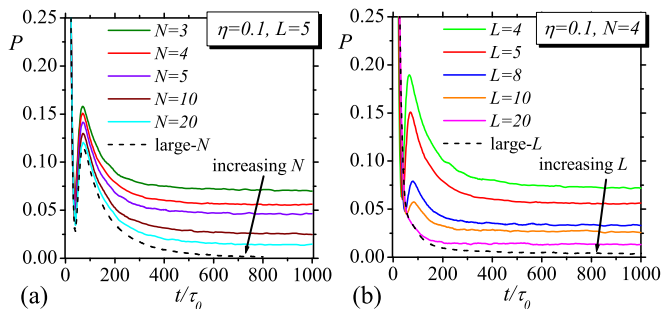


FIG. 4. Dependence of the long-time plateau value of $P(t)$ on the number of molecular sites L and number of spins per site N for $\eta = 0.1$. (a) $P(t)$ is plotted for $L = 5$ and five different N ranging from 3 to 20. For $N \rightarrow \infty$, the curves saturate at the dashed line, which is the semiclassical approximation result for the same L . (b) $P(t)$ is plotted for five different L values ranging from 4 to 20 and $N = 4$ fixed. The dashed line is the saturation curve, $N = 4$, $L \rightarrow \infty$.

Fig. 4. For fixed L and increasing N , $P(t)$ eventually saturates at the curve obtained from the semiclassical description (2) [see Fig. 4(a)]. This saturation means a total elimination of the effect of nuclear-spin dynamics for large N . The decay regime of $P(t)$ with a fixed small N and increasingly large L is less obvious. The saturation curve of $P(t)$ in Fig. 4(b) retains the long-time tail and thus differs from the result of semiclassical approximation qualitatively. This is an indication that the long-time behavior of $P(t)$ remains sensitive to the quantum dynamics of nuclear spins for $L \rightarrow \infty$.

To understand this effect, we investigate the large- L saturation curves for different N . We infer that in this regime the long-time tail of $P(t)$ slowly decays with time as $1/\sqrt{t}$ and scales with N as $1/N$. Figure 5 illustrates this dependence for $\eta = 0.1$. We further checked that this result is almost insensitive to η , at least for $\eta = 0.2 - 0.01$. However, we note that the overall amplitude of the effect is small; for $N = 2$, for example, the $1/\sqrt{t}$ decay sets up at $P(t) \approx 0.012$ (see Fig. 5).

IV. DISCUSSION

As we have shown above, the quantum dynamics of nuclear spins does not influence the initial relaxation of $P(t)$ but shows up at long times as a plateau for finite LN or as a slow decay $\sim 1/\sqrt{t}$ for $L \rightarrow \infty$.

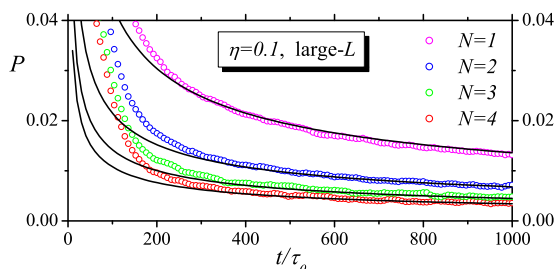


FIG. 5. Large- L saturation curves for $\eta = 0.1$ and $N = 1$ (magenta), $N = 2$ (blue), $N = 3$ (green), and $N = 4$ (red). Black lines are plotted from Eq. (6). The statistical error bars are of the order of the symbols size.

The fact that the initial decay of $P(t)$ is not affected by the nuclear-spin dynamics can be understood from the following reasoning. Defining the cumulant expansion, $P(t) = \exp[\sum_{n=1}^{\infty} K_n(t)]$, where $K_n \propto b_{\text{hf}}^n$, from Eq. (4) one can find the first nonvanishing cumulant K_2 to be

$$K_2(t) = -2b_{\text{hf}}^2 \int_0^t dt_1 \int_0^{t_1} dt_2 G_L(0, t_1 - t_2), \quad (5)$$

where $G_L(r, t)$ is the Green's function of the random walk over L sites. Equation (5) coincides with the second cumulant function obtained from the semiclassical approximation [25]. This explains why the initial relaxation is insensitive to the quantum dynamics of nuclear spin, even in the ultraquantum case $N = 1$.

Similar to the semiclassical result [25], the approximation $P(t) \approx \exp[K_2(t)]$ correctly describes the dominant spin relaxation, so that the spin relaxation time τ_S is set by $K_2(t)$ and is insensitive to the nuclear-spin dynamics. For large number of sites ($L \gg \eta^{-2/3}$) the form $P(t) \approx \exp[-(t/\tau_S)^{3/2}]$, with $\tau_S \simeq \tau_0/\eta^{4/3}$, follows from the results of previous semiclassical treatments [24,25].

Our findings for the long-time behavior of $P(t)$ can be summarized in the empirically derived formula

$$P(t) \approx \frac{1}{N} \left(\frac{1}{L} + \frac{\alpha}{\sqrt{t/\tau_0}} \right), \quad t \gg \tau_S, \quad (6)$$

where $\alpha \approx 0.43$. The combination in the parentheses in Eq. (6) is approximately the inverse number of sites visited by the carrier. Indeed, for small L and $t/\tau_0 \gg L^2$, all the L sites are visited equally many times, and the inverse number of visited sites is $1/L$. For $L \rightarrow \infty$, on the other hand, the average number of sites visited by the carrier is $\sim \sqrt{t/\tau_0}$, and thus its inverse is $\alpha/\sqrt{t/\tau_0}$. Then Eq. (6) is the inverse number of nuclear spins that couple to the carrier spin during a long-term diffusion.

To further elucidate this behavior we note that the Hamiltonian (1) conserves the z component of the total spin. Therefore the initial carrier spin polarization does not average to zero but becomes redistributed between the carrier and nuclear spins, so it is reasonable to expect that for systems with a smaller number of nuclear spins $P(t)$ can stay essentially nonzero for arbitrarily long times (in the absence of other spin relaxation mechanisms). However, the fact that this redistribution leads to a nonoscillatory, fixed or slowly changing $P(t)$ at long times is nontrivial. Moreover, the peculiar dependence (6) means that the polarization becomes evenly distributed between the carrier spin and nuclear spins which couple to the carrier spin in the course of diffusion. We should also keep in mind that the Hamiltonian (1) neglects the nuclear-spin relaxation, as well as the carrier spin relaxation, e.g., due to spin-orbit coupling, dipolar coupling to other electronic spins in the sample, or some other relaxation channels. Thus the time intervals over which the polarization dynamics is considered in this paper, including the ones we call "long times," are always shorter than the nuclear-spin relaxation and other spin relaxation times but much longer than the typical time of the hyperfine-induced relaxation of the carrier (electronic) spin.

It is also remarkable that the amplitude of the tail is almost independent of η but is determined by L and N . This independence resembles the central-spin problem ($L = 1$,

large N), where the central-spin polarization evolves into $1/3$ of its initial value regardless of the interaction strength [20,31] and relaxes from this value very slowly [29,30,33].

The treatment presented in this work excludes the energy and positional disorder. Such a disorder is characteristic of organic semiconductor systems. It leads to a wide spread in the average hopping times (instead of the single parameter τ_0) and introduces multiple time scales into the problem. On average, this disorder results in longer waiting times and, for low-energy sites, increases the probability of returns to the same sites. These factors would make the effect of the nuclear-spin dynamics more pronounced. However, a detailed examination of the joint impact of disorder and nuclear-spin dynamics would lead to technical complications and would obscure the main point of the work, the impact of the nuclear-spin dynamics. The model adopted in our current work reduces the number of relevant parameters while at the same time preserving the random character of the waiting times and thus makes it possible to understand the key features of the nuclear-spin dynamics in quantitative detail.

It is interesting to explore the role of the nuclear-spin dynamics within two- and three-dimensional transport models, although this would require much longer computation times and more computer memory. Our results suggest that the effect of nuclear-spin dynamics depends primarily on the average number of sites visited (or revisited) by the carrier. Thus one might speculate that the effect of the nuclear-spin dynamics could be important, e.g., for two- and three-dimensional

transport with deep traps (when the carrier can stay on a single site for a long time) and would be weak if the transport in two and three dimensions is free of deep traps, when the carrier quickly leaves the current site and rarely returns to this site again. However, in order to confirm or refute these speculations, separate detailed studies are needed in the future.

In conclusion, we have demonstrated that the quantum dynamics of nuclear spins leads to the long-time steady or slowly decreasing carrier spin polarization, a feature which is not captured by the semiclassical approximation. The long-time behavior extends up to the times when other relaxation mechanisms become important (e.g., carrier spin-lattice relaxation times or hydrogen nuclear-spin dephasing times). The effect can be strong for carriers diffusing over fewer molecular sites, e.g., in the situation realized in tunnel magnetoresistance experiments in organic spin valves at the onset of multiple-step tunneling [7].

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