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Hyperfine interaction and its effects on spin dynamics in organic solids

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Hyperfine interaction (HFI) and spin-orbit coupling are two major sources that affect electron spin dynamics. Here we present a systematic study of the HFI and its role in organic spintronic applications. For electron spin dynamics in disordered π -conjugated organics, the HFI can be characterized by an effective magnetic field whose modular square is a weighted sum of contact and dipolar contributions. We determine the effective HFI fields of some common π -conjugated organics studied in the literature via first-principles calculations. Most of them are found to be less than 2 mT. While the H atoms are the major source of the HFI in organics containing only the C and H atoms, many organics contain other nuclear spins, such as Al and N in tris-(8-hydroxyquinoline) aluminum, that contribute to the total HFI. Consequently the deuteration effect on the HFI in the latter may be much weaker than in the former. The HFI gives rise to multiple resonance peaks in electron spin resonance. In disordered organic solids, these individual resonances are unresolved, leading to a broad peak whose width is proportional to the effective HFI field. As electrons hop among adjacent organic molecules, they experience a randomly varying local HFI field, inducing electron spin relaxation and diffusion. This is analyzed rigorously based on master equations. Electron spin relaxation undergoes a crossover along the ratio between the electron hopping rate $\bar{\eta}$ and the Larmor frequency Ω of the HFI field. The spin relaxation rate increases (decreases) with $\bar{\eta}$ when $\bar{\eta} \ll \Omega$ ($\bar{\eta} \gg \Omega$). A coherent beating of electron spin at Ω is possible when the external field is small compared to the HFI. In this regime, the magnetic field is found to *enhance* the spin relaxation.

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I. INTRODUCTION

The field of organic spintronics has advanced rapidly since the discovery of strong magnetoresistance in organic spin-valve structures.^{1,2} Organic spintronics is largely motivated by the weak spin-orbit coupling (SOC) and hyperfine interaction (HFI) of light constituent elements³ in the organic solids that lead to a long lifetime of electron spins needed for spin manipulation. Recently the SOC and its effects on organic spintronics have been systematically quantified and studied.⁴ Yet, being another source of spin relaxation and diffusion, the two crucial properties for the spintronics application, the HFI has been less quantified. Despite the fact that HFI has been used to interpret many magnetic field-dependent phenomena including organic magnetoresistance⁵ and magnetic field-dependent luminescence⁶ in organics devices, the HFI strength in individual organics is usually treated as a fitting parameter when comparing theory and experiment.⁷ The lack of quantitative knowledge of the HFI severely hampers an accurate description of spin dynamics and reliable interpretation of experiments.

The organics used in spintronic applications are dense films made of π -conjugated molecules or oligomers, where electron conduction is via a hopping mechanism. While in simple π -conjugated molecules containing only the C and H atoms, such as benzene, the nuclear spin and the HFI essentially originate from H, many organic materials studied for spintronics also have other elements with

finite nuclear spins. The total HFI experienced by the electrons should be the contribution from all these nuclear spins. Common nuclei encountered in organic spintronics and their properties are listed in Table I.⁸ For example, in tris-(8-hydroxyquinoline) aluminum (Alq₃), one of the most frequently studied organics, N and Al nuclei have nonzero nuclear spins. A systematic evaluation of contributions from all such nuclei to the total HFI is thus needed.

Nuclear spins can be modified by substituting a given nucleus with its isotope. This substitution leaves electron wavefunction largely intact, which allows a systematic study of the HFI. In organics, the isotope effect is frequently studied by replacing H with D, i.e., deuteration.^{7,9,10} In cases where H is the only HFI source, the effect of deuteration on the HFI is straightforward. For organics with other nuclear spins, the effect of deuteration on the HFI depends on how much the HFI originates from the H atoms. In the extreme case where the contribution of H to the total HFI is zero, deuteration would not change the HFI at all.

A significant difference between organic films and inorganic solids is that two nominally identical organic films can have very different molecular arrangements or morphologies. The SOC was found to depend on the morphology significantly and may vary by orders of magnitude.⁴ It is therefore necessary to examine to what extent the molecular morphology will affect the HFI.

Spin relaxation due to the HFI in disordered systems

TABLE I: Common nuclear spins and their relevant properties to HFI in organic solids

Nucleus	Natural abundance	I	γ_N (10^7 T $^{-1}$ s $^{-1}$)
H	0.999885	1/2	26.7522
D	0.000115	1	4.1066
^{12}C	0.9893	0	
^{13}C	0.0107	1/2	6.7283
^{14}N	0.99636	1	1.9338
^{15}N	0.00364	1/2	-2.7126
^{16}O	0.99757	0	
^{17}O	0.00038	5/2	-3.6281
^{18}O	0.00205	0	
^{19}F	1.0	1/2	25.1815
^{27}Al	1.0	5/2	6.9763
^{32}S	0.9493	0	
^{33}S	0.0076	3/2	2.0557
^{33}S	0.0429	0	
^{69}Ga	0.60108	3/2	6.4389
^{71}Ga	0.39892	3/2	8.1812
^{113}In	0.0429	9/2	5.8845
^{115}In	0.9571	9/2	5.8972
^{63}Cu	0.6915	3/2	7.1118
^{65}Cu	0.3085	3/2	7.6044
^{191}Ir	0.373	3/2	0.4812
^{193}Ir	0.627	3/2	0.5227

was first studied by D'yakonov and Perel' in amorphous semiconductors.¹¹ Their picture is that an electron localized at a shallow donor precesses its spin around the local HFI field. This precession is frequently interrupted by the electron hopping (tunneling) to adjacent donors where the HFI field is randomly oriented. In their model, the electron hopping is assumed to be much faster compared with the electron precession around the HFI field. In a recent Monte Carlo simulation of electron spin diffusion in disordered organics,¹² the HFI is treated as a randomly oriented magnetic field at each molecule, where the trajectory of electron spin hopping is followed across the system. Again the study is confined to the fast hopping regime. However, in organic solids hopping rates can vary orders of magnitude. Furthermore, most experimental studies are carried out at low temperatures and in low-mobility materials such as phenylene vinylene (PPV) and Alq₃. Thus, in many situations the electron hopping is slower compared with the Larmor frequency of the HFI field. It would be useful to have a more complete understanding of the interplay between the different time scales. Moreover, in our opinion, spin relaxation and diffusion in disordered organics are not rigorously formulated in the literature, which leaves their meanings ambiguous.

In this paper, we employ first-principles calculations to quantify the HFI strengths of both electron and hole in common organics considered for organic spintronic applications. We also analyze the expected deuteration effect for these organics. A master equation is derived rigorously and solved exactly to describe the HFI effect on

spin relaxation and diffusion. The paper is organized as follows. In section II, we briefly review the HFI and its effect on electron spin resonance. We compute the HFI field for various organics in Sec. III and study the expected deuteration effect in Sec. IV. We derive a master equation based on quantum statistical physics for spin relaxation and diffusion and clarify their meanings in Sec. V. Spin relaxation and diffusion are analyzed in detail by both analytical and numerical approaches in Secs. VI and VII. Finally we summarize our results in Sec. VIII.

II. BRIEF REVIEW OF HFI

A. Isotropic and anisotropic HFIs

The HFI is between the nuclear magnetic moment $\hat{\mu}_N \equiv \gamma_N \hbar \hat{\mathbf{I}}$ and the electron magnetic moment $\hat{\mu}_e \equiv \gamma \hbar \hat{\mathbf{S}}$. Here $\hat{\mathbf{I}}$ and $\hat{\mathbf{S}}$ are nuclear and electron spins (throughout the paper, we use the hat to denote a quantum operator). γ_N and γ are magnetogyric ratios of the nucleus and electron. γ_N is directly related to the resonant frequency in nuclear magnetic resonance (NMR), $\omega_N = \gamma_N B_0$, under an external magnetic field of B_0 . In this paper we do not distinguish between γ for an electron in organics and that for a free electron because of their relatively small difference arising from the weak SOC in the π -conjugated systems.⁴ In contrast, γ_N varies significantly among different nuclei and even among different isotopes.

In organics spintronics, one is primarily concerned with the spin of mobile electrons and holes, i.e., the delocalized π electrons in the molecule or oligomer. Since these π -electron wavefunctions extend over many nuclei in the system, the HFI for the electron comes from all these nuclei. It consists of two terms.^{13,14} The first is the isotropic Fermi contact interaction,

$$H_I = \sum_{\alpha} A_{\alpha} \hat{\mathbf{I}}_{\alpha} \cdot \hat{\mathbf{S}} \equiv \sum_{\alpha} \frac{8\pi}{3} \hbar^2 \gamma_N^{\alpha} |\psi(\mathbf{r}_{\alpha})|^2 \hat{\mathbf{I}}_{\alpha} \cdot \hat{\mathbf{S}}, \quad (2.1)$$

where $\hat{\mathbf{I}}_{\alpha}$ is the α th nuclear spin, located at $\mathbf{r}_{\alpha}$, and γ_N^{α} is the magnetogyric ratio. A_{α} is proportional to the modular square of the electronic wavefunction, $|\psi(\mathbf{r}_{\alpha})|^2$, at the α th nucleus.

In addition, there is a dipolar interaction between the electron and nuclear magnetic dipoles,

$$H_D = \sum_{\alpha} \hat{\mathbf{I}}_{\alpha} \cdot \mathbf{T}^{\alpha} \cdot \hat{\mathbf{S}}, \quad (2.2)$$

where the second-rank tensor $\mathbf{T}^{\alpha}$ describes the dipolar coupling between the α th nuclear spin and the electron spin,

$$\mathbf{T}^{\alpha} = \hbar^2 \gamma_N^{\alpha} \left\langle \frac{|\mathbf{r} - \mathbf{r}_{\alpha}|^2 - 3(\mathbf{r} - \mathbf{r}_{\alpha})(\mathbf{r} - \mathbf{r}_{\alpha})}{|\mathbf{r} - \mathbf{r}_{\alpha}|^5} \right\rangle,$$

with the average $\langle \dots \rangle$ being over the whole spatial distribution of the electron wave function, $|\psi(\mathbf{r})|^2$. The trace

of the inner product of $\mathbf{T}^\alpha$ and itself, denoted as $\mathbf{T}^\alpha : \mathbf{T}^\alpha$, is invariant under rotations,

$$\mathbf{T}^\alpha : \mathbf{T}^\alpha \equiv \sum_{pp'=x,y,z} T_{pp'}^\alpha T_{pp'}^\alpha = 6\hbar^4 (\gamma\gamma_N^\alpha)^2 \left\langle \frac{1}{|\mathbf{r} - \mathbf{r}_\alpha|^6} \right\rangle, \quad (2.3)$$

and $\mathbf{T}^\alpha$ itself is traceless,

$$\text{Tr} \mathbf{T}^\alpha \equiv \sum_p T_{pp}^\alpha = 0. \quad (2.4)$$

When the dynamics of the nuclear spins is much slower than that of the electron spin, the former can be considered as frozen, or equivalently, as a static magnetic field (this is not always a good approximation in organics, and more discussions on this will be given in Sec. VI),

$$H = H_I + H_D = \hbar\gamma \mathbf{B}_H \cdot \hat{\mathbf{S}}. \quad (2.5)$$

Here the effective HFI field $\mathbf{B}_H$ is

$$\mathbf{B}_H = \mathbf{B}_I + \mathbf{B}_D, \quad (2.6)$$

with $\mathbf{B}_I$ and $\mathbf{B}_D$ being the effective magnetic field originated from the isotropic and dipolar HFIs,

$$\mathbf{B}_I = (\hbar\gamma)^{-1} \sum_\alpha A_\alpha \mathbf{I}_\alpha, \quad (2.7)$$

$$\mathbf{B}_D = (\hbar\gamma)^{-1} \sum_\alpha \mathbf{I}_\alpha \cdot \mathbf{T}^\alpha. \quad (2.8)$$

In general, the orientations of $\mathbf{B}_I$ and $\mathbf{B}_D$ for a given molecule are not correlated, and therefore the amplitude of $\mathbf{B}_H$ is

$$B_H = \sqrt{B_I^2 + B_D^2}, \quad (2.9)$$

with

$$B_I = (\hbar\gamma)^{-1} \left(\sum_\alpha A_\alpha^2 I_\alpha (I_\alpha + 1) \right)^{1/2}, \quad (2.10)$$

$$B_D = (\hbar\gamma)^{-1} \frac{1}{3} \left(\sum_\alpha (\mathbf{T}^\alpha : \mathbf{T}^\alpha) I_\alpha (I_\alpha + 1) \right)^{1/2} \quad (2.11)$$

Since the nuclear spins in organic solids are not macroscopically magnetized, the local HFI field $\mathbf{B}_H$ and therefore the electron spin precession axis at each molecule or oligomer has a random orientation. The precession frequency, though, is a constant,

$$\Omega = \gamma B_H = \hbar^{-1} \left(\sum_\alpha (A_\alpha^2 + \frac{1}{3} \mathbf{T}^\alpha : \mathbf{T}^\alpha) I_\alpha (I_\alpha + 1) \right)^{1/2}, \quad (2.12)$$

which defines the time scale of electron spin precession around the local HFI field.

B. Quantum nature of HFI

Strictly speaking, nuclear spin is a quantum property. In fact, the quantized nuclear spin is the foundation of the NMR. The quantum nature of the HFI is clearer if we express the isotropic and dipolar HFIs defined in Eqs. (2.1) and (2.2) in terms of $\hat{S}_\pm = \hat{S}_x \pm i\hat{S}_y$ and $\hat{I}_{\alpha\pm} = \hat{I}_{\alpha x} \pm i\hat{I}_{\alpha y}$,

$$H_I = \sum_\alpha A_\alpha \left[\hat{I}_{\alpha z} \hat{S}_z + \frac{1}{2} (\hat{I}_{\alpha+} \hat{S}_- + \hat{I}_{\alpha-} \hat{S}_+) \right], \quad (2.13)$$

$$H_D = \hbar^2 \gamma \sum_{\alpha, q=0, \pm 1, \pm 2} \gamma_N^\alpha \left[F_\alpha^{(q)} \Phi_\alpha^{(q)} + \text{H.c.} \right], \quad (2.14)$$

where $\Phi^{(q)}$ describe the operator portion¹³

$$\Phi_\alpha^{(0)} = -\hat{I}_{\alpha z} \hat{S}_z + \frac{1}{4} (\hat{I}_{\alpha+} \hat{S}_- + \hat{I}_{\alpha-} \hat{S}_+), \quad (2.15)$$

$$\Phi_\alpha^{(1)} = -\frac{3}{2} (\hat{I}_{\alpha z} \hat{S}_+ + \hat{I}_{\alpha+} \hat{S}_z), \quad (2.16)$$

$$\Phi_\alpha^{(2)} = -\frac{3}{4} \hat{I}_{\alpha+} \hat{S}_+, \quad (2.17)$$

and $F_\alpha^{(0)}$ the prefactor,

$$F_\alpha^{(0)} = \left\langle \frac{1 - 3 \cos^2 \theta_\alpha}{|\mathbf{r} - \mathbf{r}_\alpha|^3} \right\rangle, \quad (2.18)$$

$$F_\alpha^{(1)} = \left\langle \frac{\sin \theta_\alpha \cos \theta_\alpha e^{-i\phi_\alpha}}{|\mathbf{r} - \mathbf{r}_\alpha|^3} \right\rangle, \quad (2.19)$$

$$F_\alpha^{(2)} = \left\langle \frac{\sin^2 \theta_\alpha e^{-2i\phi_\alpha}}{|\mathbf{r} - \mathbf{r}_\alpha|^3} \right\rangle. \quad (2.20)$$

Here the polar angles are defined as $(\sin \theta_\alpha \cos \phi_\alpha, \sin \theta_\alpha \sin \phi_\alpha, \cos \theta_\alpha)^T = (\mathbf{r} - \mathbf{r}_\alpha)/|\mathbf{r} - \mathbf{r}_\alpha|$, $F_\alpha^{(-q)} = F_\alpha^{(q)*}$, and $\Phi_\alpha^{(-q)} = \Phi_\alpha^{(q)\dagger}$.

We see that in H_I a flip of the electron spin is always accompanied by a nuclear spin flop, i.e., the total spin along the quantization axis, the z -axis, is conserved, $\Delta m_F \equiv \Delta(m_I + m_S) = 0$. In H_D , however, an electron spin flip can couple to a nucleus with a nuclear spin flop, no change, or spin flip, $\Delta m_F = 0, \pm 1$, and ± 2 . This distinction becomes particularly important when discussing the nuclear spin relaxation caused by the electron spin dynamics, for processes with different Δm_F require different energies. In contrast, when the HFI is treated as a classical field, it is immaterial to distinguish between H_I and H_D .

C. Electron spin resonance

In the absence of HFI, electron spin resonance (ESR) takes place at frequency $\omega_0 = \gamma B_0$, where B_0 is the external magnetic field. The HFI interacts with the electron spin and the interaction strength depends on the state

of the nuclear spin. Since a nuclear spin can only take quantized values, a spin resonance is split into several peaks.

If we ignore temporarily the dipolar interaction, the electron and nuclear spin quantization axes are along the same direction, i.e., along the external magnetic field, which is assumed to be the z -axis throughout this paper,

$$H = \hbar\gamma B_0 \hat{S}_z + \hat{S}_z \sum_{\alpha} A_{\alpha} \hat{I}_{\alpha z}. \quad (2.21)$$

Here we neglect the Zeeman energy of the nuclear spin since γ_N is three orders of magnitude smaller than γ . The states are characterized by $m_S = \pm 1/2$ and m_I along the electron and nuclear spin quantization axes. The frequency of the spin resonance, presumably due to the transition between $m_S = 1/2$ and $-1/2$, would be dependent on the quantized nuclear spin states

$$\omega = \gamma B_0 + \hbar^{-1} \sum_{\alpha} A_{\alpha} m_{\alpha} \equiv \omega_0 + \Delta\omega(\{m_{\alpha}\}), \quad (2.22)$$

where m_{α} is the magnetic quantum number of the nuclear spin $\hat{I}_{\alpha}$.

If the resonance lines are very narrow in the frequency domain, the HFI will give rise to several lines corresponding to different nuclear magnetic quantum numbers, as usually happens in solution.¹³ In contrast, the ESR lines in organic solids are usually not resolved, with different ESR lines lumping together, forming a broad peak whose width can be estimated by

$$\langle(\Delta\omega)^2\rangle = \hbar^{-2} \sum_{\alpha} A_{\alpha}^2 \langle m_{\alpha}^2 \rangle = \frac{1}{3\hbar^2} \sum_{\alpha} A_{\alpha}^2 I_{\alpha}(I_{\alpha} + 1). \quad (2.23)$$

When the dipolar interaction is included, the magnetic field experienced by the α th nuclear spin, $\hat{I}_{\alpha}$, is mainly from the HFI of the electron, $\mathbf{B}_e^{\alpha}$, which, for the electron spin $m_S = \pm 1/2$, is

$$\gamma_N^{\alpha} \mathbf{B}_e^{\alpha} = \pm \frac{1}{2\hbar} (T_{zx}^{\alpha}, T_{zy}^{\alpha}, T_{zz}^{\alpha} + A_{\alpha})^T, \quad (2.24)$$

and its orientation is the quantization axis of the nuclear spin. Since the ESR is between electron spin states $m_S = \pm 1/2$ for a given set of nuclear spins, $\{m_{\alpha}\}$, the resonance frequency in the presence of both H_I and H_D is

$$\begin{aligned} \omega &= \gamma B_0 + 2 \sum_{\alpha} m_{\alpha} \gamma_N^{\alpha} |\mathbf{B}_e^{\alpha}| \\ &= \gamma B_0 + \hbar^{-1} \sum_{\alpha} m_{\alpha} \sqrt{(T_{zx}^{\alpha})^2 + (T_{zy}^{\alpha})^2 + (T_{zz}^{\alpha} + A_{\alpha})^2}. \end{aligned}$$

The overall broadening due to the HFI becomes

$$\begin{aligned} \langle(\Delta\omega)^2\rangle &= \frac{1}{\hbar^2} \sum_{\alpha} \langle m_{\alpha}^2 \rangle \langle (T_{zx}^{\alpha})^2 + (T_{zy}^{\alpha})^2 + (T_{zz}^{\alpha} + A_{\alpha})^2 \rangle \\ &= \frac{1}{\hbar^2} \sum_{\alpha} \frac{1}{3} I_{\alpha}(I_{\alpha} + 1) \left[A_{\alpha}^2 + \frac{1}{3} (\mathbf{T}^{\alpha} : \mathbf{T}^{\alpha}) \right] \\ &= \frac{1}{3} \gamma^2 B_H^2. \end{aligned} \quad (2.25)$$

Thus, the ESR line width is directly related to the effective HFI field B_H defined in Eq. (2.9). It is important to point out, though, that the ESR line width has other contributions such as dipolar and exchange couplings between electron spins, SOC, and inhomogeneous broadening.¹⁴

As we will show in Sec. V, the electron spin relaxation and diffusion, based on both classical and quantum treatments, can also be characterized by B_H .

III. STRENGTHS OF HFI IN ORGANICS

In π -conjugated molecules or oligomers, charge carriers are electron and hole polarons, i.e., electron and hole surrounded by the lattice distortion, which are nothing but the HOMOs in a negatively and positively charged molecule or oligomer with a self-consistently determined molecular geometry due to the extra charge. The HFI strengths calculated here are for these HOMO states. We emphasize that both the HFI and SOC strengths depend strongly on the wavefunction of the electronic states. In particular, for deep traps that are far from the HOMO states in energy, their HFI and SOC are completely unrelated to those in the polaron states.

In simple π -conjugated organics such as benzene, the π -orbital gives not only zero unpaired electron density at the carbon atoms, but also zero electron density at the nearby hydrogen atoms. Thus, if one takes into account only the π electrons, the isotropic Fermi contact interaction would be zero. The finite HFI value in a π -conjugated organic molecule is due to the configurational mixing between the π and σ orbitals.¹⁵ The σ orbitals are also essential for properly describing the SOC in organics.⁴

Because of the many-body nature of the configurational mixing, it is not trivial to use a first-principles approach to reliably compute the HFI. Although in principle, the contact HFI at different nuclei can be estimated from the Mulliken spin population analysis, it suffers from low accuracy and somewhat arbitrariness. Recently the encouraging performance of the density functional theory (DFT) with hybrid functionals (partial inclusion of the Hartree-Fock exchange) has been demonstrated by many applications. The combination of such hybrid functionals with carefully optimized basis sets gives excellent computational result for the HFI constant.

In this work the GAUSSIAN09 program suite¹⁶ is used to carry out the HFI calculations for representative organic materials for electron- and hole-polaron states, since it is one of the very few first-principles packages that allows one to reliably compute both the contact and dipolar interactions at different atoms in organic molecules. We use the hybrid density functional B3LYP with Becke's three parameter exchange¹⁷ and the nonlocal correlation of Lee, Yang and Parr,¹⁸ as well as the DFT-optimized valence triple-zeta basis TZVP¹⁹ for our calculations of the HFIs. The combination of the B3LYP

functional and the TZVP basis has been shown to give excellent prediction of the HFIs for radicals of moderate and large size that include the first, second, and third row nuclei.²⁰ For elements beyond the third row, we use the Stuttgart/Dresden effective core potentials.²¹ All the HFI calculations were performed at the optimized geometries obtained at the B3LYP/6-31+G(d) level of theory due to its relatively low computational cost for larger radicals. Test calculations have shown that this makes negligible difference from the structures optimized at the more demanding B3LYP/TZVP level of theory.

For the HOMO state of a given molecule, the GAUSSIAN09 suite can provide A_α and T^α for the α th atom in the molecule. We then use Eqs. (2.9)-(2.11) to calculate the effective HFI values of B_I , B_D , and B_H for the molecule.

A. Organics containing only H nuclear spin

We start with simple organics containing only the C and H atoms. C has two isotopes, ^{12}C with no nuclear spin and ^{13}C with a nuclear spin of $I = 1/2$. Since the natural abundance of ^{12}C is close to 99%, the contribution from the C atoms to the HFI usually can be neglected. The only exception in our examples is C_{60} and its derivatives, where a residual ^{13}C is the sole (or major) source of the HFI. The other important element is H which has a nuclear spin of $1/2$ and a particularly large γ_N . For many simple π -conjugated materials, H is essentially the only source of the HFI.

Table II summarizes the total HFI field B_H and its contact and dipolar contributions, B_I and B_D , for this type of spintronic materials. We also list some organics containing other elements, such as O in DOO-PPV and S in T_6 . However, since naturally abundant O and S do not have nuclear spins, the HFI in these organics is due solely to the H atoms.

Before we discuss the obtained HFI fields in Table II for individual organics, we compare our calculations with well-documented experimental data of the HFI strengths in benzene cation²² and C_{60} anion.²³ For benzene cation, the removal of one electron causes a Jahn-Teller distortion of molecular structure from D_{6h} to D_{2h} symmetry. The experimental measured isotropic HFI constants are $A_1 = A_4 = -0.82$ mT and $A_2 = A_3 = A_5 = A_6 = -0.24$ mT. The measured anisotropic HFI tensors along corresponding principal axes are: $T_{11} = 0.45$ mT, $T_{22} = -0.51$ mT, and $T_{33} = 0.06$ mT for atoms 1 and 4; $T_{11} = -0.12$ mT, $T_{22} = 0.24$ mT, and $T_{33} = -0.12$ mT for atoms 2, 3, 5, and 6. Using Eqs. (2.10) and (2.11), we obtain, based on the experimental values, $B_I = 1.09$ mT and $B_D = 0.56$ mT. For C_{60} anion, the measured isotropic HFI constant due to ^{13}C is $A = 0.006$ mT, and the corresponding field is $B_I = 0.0052$ mT. For both materials the agreement between experiment and theory is satisfactory with theoretical results slightly larger than the experimental values.

From Table II, we see that the methyl (CH_3) radical, which has a planar structure with three equivalent H atoms, has the largest HFI among this kind of π -conjugated organics. This is reasonable because the π electron in CH_3 is the most localized (at a single C atom) with the largest possible number (three) of adjacent H atoms. In longer π -conjugated organics, each C atom is usually bonded with one H atom and the π electrons are delocalized over many C atoms. Consequently, the HFI in these materials should be weaker¹⁵ than that in CH_3 .

The high mobility pentacene and rubrene have rather small HFI strengths, which can be attributed to the delocalization in their planar structures. This delocalization effect also manifests itself in the difference between benzene and biphenyl. The biphenyl molecule is comprised of two phenyl rings linked by a C-C bond. Because the wavefunction of the π electron is delocalized in the two rings, the HFI of the electron, 0.98 mT, is smaller than that in benzene, 1.27 mT. The frequently studied 2,5-diethyloxy poly(*p*-phenylene vinylene) (DOO-PPV) has the HFIs of 1.36 mT for the electron and 1.41 mT for the hole polaron, which are consistent with values from early magnetic resonance study,²⁴ but much smaller than the recently estimated HFI value by fitting the experiment to simple models, 6 mT.⁷ This suggests that the models there might be oversimplified.

Among these materials, C_{60} has the lowest HFI strength, 0.01 mT for both the electron and hole polarons, which originates from ^{13}C . Another material with very small HFI values (0.05 mT for electrons and 0.13 mT for holes) is [6,6]-phenyl-C61-butyric acid methyl ester (PCBM), which is C_{60} decorated by a side chain with CH groups. The reason of this diminishing HFI in PCBM is that both electron and hole polarons are still primarily localized inside C_{60} and their distribution on the side chain is vanishingly small. In literature, it was often argued that the HFI in PCBM may be strong because of the presence of the side chain with H atoms. This is not the case according to our calculation.

Another interesting observation is that in C_{60} and PCBM, the dipolar HFI dominates the isotropic contribution. The dipolar contribution in other organic materials, in general, is not very small as compared to the contact contribution. In the literature of organic spintronics, the HFI models usually consider only the isotropic contribution, which would significantly underestimate the HFI in many organic materials.

Molecular geometry has been shown to have a significant impact on the SOC whose values may be changed by orders of magnitude.⁴ Similarly one may argue that varying geometry can change the electron wavefunction, which will modify the HFI. Figure 1 shows the HFI strength in biphenyl as a function of the torsion angle between the two phenyl rings. While the change in the HFI (up to 10–20%) is noticeable, it is rather small as compared with the change in the SOC due to torsion.⁴ Therefore the HFI strength is relatively insensitive to the molecular packing in organic solids.

TABLE II: Effective HFI field (mT) for electron and hole polarons in organic solids where nuclear spins are due to H and ^{13}C .

Material	electron			hole		
	B_H	B_I	B_D	B_H	B_I	B_D
methyl radical	3.82	3.41	1.73			
benzene	1.27	1.19	0.67	1.55	1.35	0.77
DOO-PPV	1.36	1.31	0.33	1.41	1.39	0.26
sexithiophene (T_6)	0.39	0.35	0.15	0.50	0.44	0.24
rubrene	0.38	0.33	0.19	0.39	0.35	0.19
biphenyl	0.98	0.89	0.42	1.06	0.93	0.50
PCBM	0.051	0.014	0.048	0.13	0.10	0.08
C_{60}	0.01	0.006	0.009	0.01	0.002	0.01
pentacene	0.90	0.81	0.39	1.00	0.91	0.42

B. Organics with other nuclear spins

Many organics studied in the literature of organic spintronics also contain other nuclear spins. For example, in Alq_3 , one of the most commonly studied materials in the field of organic spintronics, both N and Al have nuclear spins that contribute to the total HFI. In these materials, however, the contributions from different nuclear spins are not equal but sensitive to the electron wavefunction distributions at the nuclei.

Table III summarizes the HFI strengths for this type of materials. We also list the percentage contribution from H to the total HFI. In these materials the HFI is typically between 1 and 2 mT. The only exception is CuPc , where the valence electron occupies the $3d$ orbitals of Cu, which has a strong HFI with the Cu nuclear spin. The contribution from H varies dramatically among different materials and even between the electron and hole polarons in the same material. In particular, in $\text{N,N-bis(n-hepta uorobutyl)-3,4,9,10-perylene tetracarboxylic diimide}$ (PTCDI-C4F7), a newly synthesized high-mobility organic,²⁵ the electron HFI comes mainly from H, but the hole HFI comes exclusively from F.

Among the group of Alq_3 , Inq_3 and GaQ_3 , the HFI strengths are around 1-2 mT and display no simple trend as a function of the weight of the central metal element. In contrast, the calculated SOC strength increases with the weight. Another interesting observation is that in compounds like tris(2-phenylpyridine)iridium (Irppy_3) and bis[2-(4,6-difluorophenyl)pyridinato- C_2N](picolinato)iridium (FIR-Pic), the heavy Ir atom essentially does not contribute to the HFI.

IV. DEUTERATION EFFECTS

The HFI can be modified through substituting a given nucleus with its isotope. This process changes both the nuclear spin and magnetogyric ratio, but leaves the electronic wavefunctions intact. Thus the HFI can be sys-

TABLE III: The effective HFI field B_H (mT) and H contribution p_H (%) to the total HFI in organics with other nuclear spins. *fac* and *mer* represent facial and meridional isomers, respectively.

Material	electron		hole	
	B_H	p_H	B_H	p_H
Alq_3	1.24	52.22	1.22	30.75
Inq_3	1.07	55.56	0.74	99.54
GaQ_3	1.57	21.43	2.22	9.63
PPy	2.52	81.24	1.28	90.61
PANI	1.06	99.56	2.07	47.86
CuPc	25.73	0.00	25.73	0.00
PTCDIC4F7	0.36	93.95	2.54	0.00
<i>fac</i> - Irppy_3	0.83	42.84	0.41	77.67
<i>mer</i> - Irppy_3	0.87	40.78	0.60	98.42
<i>fac</i> -FIRPic	1.35	16.77	0.95	29.61
<i>mer</i> -FIRPic	1.30	15.46	1.00	26.53

FIG. 1: (Color online) Total effective HFI field $|B_H|$ as a function of torsion in biphenyl for electron (black) and hole (red) polarons.

tematically modified for a same polaron spin.

In organic spintronics, isotope effects are usually studied by replacing H with D via deuteration. Experimentally two materials have been intensively studied: One is DOO-PPV and the other is Alq_3 . In DOO-PPV, according to our calculations, upon deuteration the HFI changes from 1.36 to 0.44 mT for the electron polaron and from 1.41 to 0.46 mT for the hole polaron. In DOO-PPV and other materials where the HFI originates solely from the H atoms, deuteration is expected to alter the HFI from B_H^H to B_H^D , with the ratio

$$\frac{B_H^H}{B_H^D} = \frac{\gamma_N^H}{\gamma_I^D} \left(\frac{I_H(I_H + 1)}{I_D(I_D + 1)} \right)^{1/2} = 3.1. \quad (4.1)$$

The experimental data on the deuteration effect in Alq_3 are quite complicated and, depending on the properties, the deuteration may¹⁰ or may not⁹ have much effect. In Alq_3 , as discussed earlier, the HFI comes from

TABLE IV: Effective HFI field B_H^D (mT) of deuterated organics and the ratio B_H^H/B_H^D in organics with other nuclear spins

Material	electron		hole	
	B_H^D	B_H^H/B_H^D	B_H^D	B_H^H/B_H^D
Alq ₃	0.88	1.40	1.03	1.19
Inq ₃	0.74	1.44	0.19	3.86
Gaq ₃	1.40	1.12	2.11	1.05
PPY	1.23	2.05	0.50	2.57
PANI	0.27	3.87	1.53	1.35
CuPc	25.73	1.00	25.73	1.00
PTCDIC4F7	0.13	2.89	2.54	1.00
<i>fac</i> -Irppy3	0.64	1.29	0.21	1.92
<i>mer</i> -Irppy3	0.68	1.27	0.17	3.59
<i>fac</i> -FIrPic	1.24	1.09	0.81	1.18
<i>mer</i> -FIrPic	1.20	1.08	0.87	1.15

three sources: N, Al, and H. Upon replacing H by D, the change in the HFI would depend on the weight of H contribution to the total HFI. In Alq₃, we find that for the electron polaron, the contributions to the HFI from N, Al, and H are 27%, 21%, and 52%, respectively, and the total HFI changes from 1.48 mT to 0.88 mT after deuteration, corresponding to a ratio of $B_H^H/B_H^D = 1.40$. For the holes, the contribution from the three elements are, 0.2% from N, 69% from Al, and 41% from H, and the HFI changes from 1.22 mT to 1.03 mT, corresponding to $B_H^H/B_H^D = 1.19$, which is rather small. Thus it would be surprising that a large deuteration effect could be seen in Alq₃.

In Table IV, we list the expected HFI change upon deuteration in various organics. In PTCDIC4F7, the HFI for the hole polaron does not change at all.

Since molecular packing during the material preparation can affect material properties, a change in the material properties upon deuteration does not necessarily indicate the importance of the HFI. Conversely, the absence of any deuteration effect does not necessarily mean that the HFI does not play any role. Thus, to unequivocally determine the significance of the HFI, one must quantitatively compare experiment with the expected isotope effects in Table IV.

V. HFI AND SPIN DYNAMICS

In organic solids, electron motion can be described by hopping among adjacent molecules. At different sites, nuclear spins are randomly oriented and so is the effective HFI field $\mathbf{B}_H$. The magnitude $|\mathbf{B}_H|$, though, is constant. Usually the HFI field is approximated by a frozen field. This approximation is valid only if the time scale for the electron precession in the HFI field of the nuclear spin is much shorter than that of the nuclear spin precession in the HFI field of electron spin, i.e., $\Omega \gg \omega_I$. ω_I can be estimated by the HFI field experienced by the individual

nuclei,

$$\gamma_N^\alpha \mathbf{B}_\alpha^e = \hbar^{-1} (A_\alpha \mathbf{S} + \mathbf{T}^\alpha \cdot \mathbf{S}) \quad (5.1)$$

and the corresponding nuclear spin precession frequency,

$$\omega_I = \gamma_N^\alpha |\mathbf{B}_\alpha^e| = \hbar^{-1} \left(\frac{3}{4} A_\alpha^2 + \frac{1}{4} \mathbf{T}^\alpha : \mathbf{T}^\alpha \right)^{1/2}, \quad (5.2)$$

where $\mathbf{S}^2 = S(S+1) = 3/4$ has been used. Comparing the above expression to Eq. (6.16), we see that $\Omega \sim \sqrt{N} \omega_I$, where N is number of nuclei over which the electron wavefunction extends. In organics where the wavefunction is localized within a molecule or oligomer, N is between 1 and 100. The approximation $\Omega \gg \omega_I$ may break down when the polaron states are relatively localized. However, treating both nuclear and electronic spins on an equal footing is beyond the scope of this paper.

In discussing the spin relaxation so far, it is always assumed that electron hopping is much faster than electron precession around the HFI field, which is roughly 1 mT, corresponding to $\Omega = 2 \times 10^8$ Hz. However, in organics the carrier mobility is very low, resulting in a smaller hopping rate that may be even slower than the HFI. For example, for Alq₃ with $\mu \simeq 10^{-6}$ cm²/Vs, at temperature of 30 K, the hopping probability is estimated to be

$$\eta = \frac{\mu k_B T}{ea^2} = 2.5 \times 10^5 \text{ s}^{-1}, \quad (5.3)$$

which is much smaller than Ω . Here a is the distance between adjacent molecules, $a \sim 1$ nm.

In organic spintronics, spin relaxation and diffusion are frequently treated kinetically as in spin chemistry,²⁶ where very few spins are present in a system far from equilibrium. In a spintronic device structure, however, many carriers are present at the steady-state. Electron spins in such a system are more appropriately described by the (spin-dependent) electrochemical potentials.^{4,27} We will consider spin relaxation and diffusion in a system with the presence of many electron spins.

The Hamiltonian of the problem is

$$\begin{aligned} H = & \sum_{is} E_i a_{is}^\dagger a_{is} + \sum_{iss'} \frac{\hbar}{2} a_{is}^\dagger \hat{\sigma}_{ss'} a_{is'} \cdot (\omega_0 \mathbf{e}_z + \mathbf{\Omega}_i) \\ & + \sum_{\langle ij \rangle s} V_{ij} (a_{is}^\dagger a_{js} + \text{H.c.}) \end{aligned} \quad (5.4)$$

Here $a_{is}^\dagger$ creates a polaron (an electron or hole with local lattice distortion) at site i with spin s and E_i is the polaron energy. $\hbar \omega_0 \mathbf{e}_z$ is the Zeeman splitting between the up and down electron spins in the presence of an external magnetic field along the z -axis. V_{ij} is the hopping integral between sites i and j and $\langle ij \rangle$ indicates the summation is limited to adjacent sites. The electron spin operator is $\hat{\mathbf{S}}_i = a_{is}^\dagger \hat{\sigma}_{ss'} a_{is'}/2$ with $\hat{\sigma}_{ss'}$ being the Pauli matrices. The HFI field at site i is

$$\mathbf{\Omega}_i = \Omega (\sin \theta_i \cos \phi_i, \sin \theta_i \sin \phi_i, \cos \theta_i)^T. \quad (5.5)$$

Since the polarons are assumed to be localized in every molecule or oligomer with the polaron motion described by hopping, by definition the hopping should be considered a perturbation, $H = H_0 + H_{\text{int}}$,

$$H_{\text{int}} = \sum_{\langle ij \rangle s} V_{ij} (a_{is}^\dagger a_{js} + \text{H.c.}). \quad (5.6)$$

We describe the system by the spin-polarized density matrix at individual sites, $\hat{\rho}_i$, as

$$\hat{\rho}_i = \rho_i^0 \frac{1}{2} (\hat{1} + \hat{\sigma} \cdot \mathbf{M}_i). \quad (5.7)$$

Here ρ_i^0 is the polaron occupation at site i and $\mathbf{M}_i$ is the spin polarization (magnetization), which is proportional to the spin-polarized electrochemical potential and is a suitable property to describe the many-electron transport problem.⁴ The magnetic moment at site i is

$$\mathbf{m}_i = Tr(\frac{\gamma \hbar}{2} \hat{\sigma} \hat{\rho}_i) = \frac{\gamma \hbar}{2} \rho_i^0 \mathbf{M}_i. \quad (5.8)$$

The spin dynamics can be studied by solving the Redfield equation of the density matrix

$$\begin{aligned} \frac{d\hat{\rho}_i^*}{dt} &= -\frac{i}{\hbar} [H_{\text{int}}^*, \hat{\rho}_i^*(0)] \\ &- \frac{1}{\hbar^2} \int_0^\infty d\tau \overline{[H_{\text{int}}^*(t), [H_{\text{int}}^*(t+\tau), \hat{\rho}_i^*]]}, \end{aligned} \quad (5.9)$$

where $\hat{A}^* = e^{iH_0 t/\hbar} \hat{A} e^{-iH_0 t/\hbar}$ is the quantum operator $\hat{A}$ in the interaction representation and the line in the integrand represents temporal average. Since the first-order term $[H_{\text{int}}^*, \hat{\rho}_i^*]$ vanishes and the hopping rate η_{ij} between sites i and j can be expressed as

$$\eta_{ij} = \frac{1}{\hbar^2} \int_0^\infty d\tau \overline{H_{\text{int}}^*(t) H_{\text{int}}^*(t+\tau)} e^{i(E_j - E_i)\tau/\hbar}, \quad (5.10)$$

we obtain

$$\rho_i^0 \frac{d\mathbf{M}_i}{dt} = \sum_i \rho_i^0 \mathbf{M}_i \times (\omega_0 \mathbf{e}_z + \boldsymbol{\Omega}_i) - \sum_j (\rho_i^0 \eta_{ij} \mathbf{M}_i - \rho_j^0 \eta_{ji} \mathbf{M}_j). \quad (5.11)$$

Here we have used

$$\begin{aligned} \frac{d\hat{\rho}}{dt} &\equiv \frac{d}{dt} e^{-iH_0 t/\hbar} \hat{\rho}^* e^{-iH_0 t/\hbar} \\ &= -\frac{i}{\hbar} [\hat{H}_0, \hat{\rho}] + e^{-iH_0 t/\hbar} \frac{d\hat{\rho}^*}{dt} e^{-iH_0 t/\hbar}. \end{aligned}$$

Equation (5.11) can be understood as the conservation of the total magnetic moment: the change in the magnetic moment at a given site is caused by its precession around the local magnetic field, the magnetic moment (carried by the electron) at this site hopping to other sites, and magnetic moments at other sites hopping into this site.

When the charge distribution in the system reaches equilibrium, from the detailed balance condition $\rho_i^0 \eta_{ij} = \rho_j^0 \eta_{ji}$, we obtain the following spin transport equation,

$$\frac{d\mathbf{M}_i}{dt} = \sum_i \mathbf{M}_i \times (\omega_0 \mathbf{e}_z + \boldsymbol{\Omega}_i) - \sum_j \eta_{ij} (\mathbf{M}_i - \mathbf{M}_j). \quad (5.12)$$

We emphasize that the hopping term in the above rate equation is quite different from that in the master equation obtained for charge transport,

$$\frac{d\rho_i^0}{dt} = - \sum_j (\eta_{ij} \rho_i^0 - \eta_{ji} \rho_j^0). \quad (5.13)$$

In the absence of spin precession, the equilibrium of magnetization, according to Eq. (5.12), is that the magnetization (or spin-polarized electrochemical potential) is uniform across the system. Whereas the equilibrium of charge density is the detailed balance, $\rho_i^0 \eta_{ij} = \rho_j^0 \eta_{ji}$, which is equivalent to a common Fermi level across the system. Equation (5.12) dictates electron spin dynamics in the presence of polaron hopping and HFI. In deriving this equation, we have treated the HFI as a frozen magnetic field. Both spin relaxation and diffusion can be studied by solving this equation.

To measure spin relaxation experimentally a quasi homogeneous spin polarization in a sample is created (as in ESR) and one watches the decay of the global spin polarization. Accordingly, we can write the spin polarization as

$$\mathbf{M}_i = \mathbf{M} + \delta \mathbf{M}_i \quad (5.14)$$

with $\mathbf{M} = \mathcal{N}^{-1} \sum_i \mathbf{M}_i$ and $\mathcal{N}$ being the number of molecules in a system. The spin relaxation time T_1 can be obtained by studying the time evolution of the following equation

$$\mathbf{M}(t) \simeq \mathbf{M}(t=0) e^{-t/T_1}. \quad (5.15)$$

For spin diffusion, experimentally an electron spin imbalance is created at one place and one tries to find at a distance how much the spin imbalance survives. It is thus a steady-state solution to a spatially inhomogeneous spin polarization. The local spin polarization is expressed as

$$\mathbf{M}_i = \bar{\mathbf{M}}_i + \delta \mathbf{M}_i, \quad (5.16)$$

where $\bar{\mathbf{M}}_i$ is the local average and $\delta \mathbf{M}_i$ is the fluctuation at the perpendicular direction whose average is zero. The spin diffusion length L_s is defined through the following differential equation

$$\nabla^2 \bar{\mathbf{M}}_i - \frac{\bar{\mathbf{M}}_i}{L_s^2} = 0, \quad (5.17)$$

or a difference equation in a three dimensional cubic lattice,⁴

$$\sum_j \eta_{ij} \left[(\bar{\mathbf{M}}_i - \bar{\mathbf{M}}_j) - \frac{a^2}{6L_s^2} \bar{\mathbf{M}}_i \right] = 0 \quad (5.18)$$

with a being the lattice constant in a cubic lattice.

Hence, to properly study spin relaxation and diffusion, one must set up the problem correctly and to reduce the general equation Eq. (5.12) into specific Eqs. (5.15) for

spin relaxation and into (5.18) for spin diffusion, respectively. In general the master equations can be solved exactly for a given lattice because they are linear. Compared with the Monte Carlo simulations, this master-equation approach has both physical clarity and guaranty of convergence.²⁸ In Eq. (5.12), there are three time scales, $1/\omega_0$ of the external field, $1/\Omega$ of the HFI, and $1/\eta$ of the polaron hopping. We will explore all the parameter ranges to elucidate the spin relaxation and diffusion behaviors in various regimes.

VI. SPIN RELAXATION

As we have discussed earlier, spin relaxation concerns how fast a homogeneous spin polarization decays over time. This can be achieved by ESR and optically excited ESR. As we will show below, spin relaxation can have drastically different behaviors due to the interplay between the polaron hopping and the HFI field.

A. Slow hopping

When the polaron hopping is very slow compared with the electron spin precession around the local field, the former can be considered as a small disturbance to the latter. The local magnetic field at site i is the sum of the external magnetic field and the local HFI field,

$$\gamma \mathbf{B}_i = \omega_0 \mathbf{e}_z + \mathbf{\Omega}_i \equiv \omega_i \mathbf{n}_i, \quad (6.1)$$

where the electron spin precession frequency is

$$\omega_i = \sqrt{\omega_0^2 + \Omega^2 + 2\omega_0\Omega \cos \theta_i}, \quad (6.2)$$

and the precession axis is

$$\mathbf{n}_i = \frac{1}{\omega_i} (\Omega \sin \theta_i \cos \phi_i, \Omega \sin \theta_i \sin \phi_i, \Omega \cos \theta_i + \omega_0)^T. \quad (6.3)$$

When the polaron-hopping term is turned off in Eq. (5.12), the magnetization at site i , denoted as $\mathbf{M}_i^0$, will precess around the total magnetic field $\mathbf{B}_i$,

$$\frac{d\mathbf{M}_i^0}{dt} = \mathbf{M}_i^0 \times \omega_i \mathbf{n}_i. \quad (6.4)$$

If at $t = 0$, a homogeneous magnetization is set along the z -axis, $\mathbf{M}_i^0(t=0) = M_0 \mathbf{e}_z$, the solution of the above differential equation is

$$\begin{aligned} \mathbf{M}_i^0(t) = & (\mathbf{M}_0 \cdot \mathbf{n}_i) \mathbf{n}_i + [\mathbf{M}_0 - (\mathbf{M}_0 \cdot \mathbf{n}_i) \mathbf{n}_i] \cos \omega_i t \\ & + \{[\mathbf{M}_0 - (\mathbf{M}_0 \cdot \mathbf{n}_i) \mathbf{n}_i] \times \mathbf{n}_i\} \sin \omega_i t. \end{aligned} \quad (6.5)$$

Without electron hopping, electron spin will precess around the local field coherently forever, and the relaxation time is infinite.

When the polaron hopping between adjacent sites is included, finding a general solution to Eq. (5.12) is difficult. However, since the hopping is assumed to be slow, we can seek the solution with the following form,

$$\mathbf{M}_i(t) = \mathbf{M}_i^0(t) A(t), \quad (6.6)$$

where $A(t)$ is a slow-varying function of time resulted from hopping. Substituting Eq. (6.6) into Eq. (5.12), we obtain the differential equation of $A(t)$,

$$\frac{1}{A} \frac{dA}{dt} \mathbf{M}_i^0 = - \sum_j \eta_{ij} (\mathbf{M}_i^0 - \mathbf{M}_j^0), \quad (6.7)$$

with its solution being

$$A(t) = A(0) e^{-t/\tau}, \quad (6.8)$$

$$\tau^{-1} = \sum_j \eta_{ij} \left(1 - \frac{\mathbf{M}_i^0 \cdot \mathbf{M}_j^0}{|\mathbf{M}_i^0|^2} \right). \quad (6.9)$$

The macroscopic spin polarization of the system is then

$$\mathbf{M}(t) = \frac{1}{N} \sum_i \mathbf{M}_i(t) = \frac{1}{N} \sum_i \mathbf{M}_i^0(t) e^{-t/\tau}. \quad (6.10)$$

We will use Eq. (6.10) together with Eq. (6.9) to determine the spin relaxation time in the slow-hopping regime.

1. Zero external magnetic field

From the above equation, if $\mathbf{M}_i^0(t)$ is independent of time, the spin relaxation time T_1 would be τ . However, it is possible that the macroscopic $\sum_i \mathbf{M}_i^0(t)$ varies with time and this temporal modulation survives the average among different sites, which would lead to a coherent beating in the time domain. The time-dependent beating can be clearly seen at $\omega_0 = 0$, i.e., in the absence of the external field, where $\omega_i = \Omega$ and $\mathbf{n}_i = \mathbf{\Omega}/\Omega$. According to Eq. (6.5),

$$\begin{aligned} \frac{M_{ix}^0}{M_0} &= \sin \theta_i \cos \theta_i \cos \phi_i (1 - \cos \Omega t) - \sin \theta_i \sin \phi_i \sin \Omega t, \\ \frac{M_{iy}^0}{M_0} &= \sin \theta_i \cos \theta_i \sin \phi_i (1 - \cos \Omega t) + \sin \theta_i \cos \phi_i \sin \Omega t, \\ \frac{M_{iz}^0}{M_0} &= \cos^2 \theta_i + \sin^2 \theta_i \cos \Omega t. \end{aligned} \quad (6.11)$$

Since the ensemble average yields

$$\begin{aligned} \left\langle \frac{\mathbf{M}_i^0 \cdot \mathbf{M}_j^0}{|\mathbf{M}_i^0|^2} \right\rangle &= \left\langle \frac{M_{iz}^0 M_{jz}^0}{M_0^2} \right\rangle \\ &= \langle \cos^2 \theta_i \cos^2 \theta_j + \frac{1}{2} \sin^2 \theta_i \sin^2 \theta_j \rangle = \frac{1}{3}, \end{aligned} \quad (6.12)$$

we have, from Eq. (6.9),

$$\tau^{-1} = \frac{2}{3} \sum_j \eta_{ij} \simeq 4\bar{\eta}, \quad (6.13)$$

where we consider a cubic lattice with every site having 6 adjacent neighbors. The time evolution of the spatially averaged electron spin is described by, according to Eq. (6.10),

$$\mathbf{M}(t) = \frac{1}{N} \sum_i M_{iz}(t) \mathbf{e}_z = \frac{1}{3} M_0 (1 + 2 \cos \Omega t) e^{-t/\tau} \mathbf{e}_z. \quad (6.14)$$

Thus the spin relaxation rate for the envelop function ($\cos \Omega t = 1$) is

$$T_1^{-1} = \tau^{-1} \simeq 4\bar{\eta}. \quad (6.15)$$

Equation (6.15) indicates that in the slow-hopping regime, the polaron hopping *facilitates* spin relaxation.

2. Small magnetic field, $\omega_0 < \Omega$

It is interesting to examine whether the coherent beating at frequency Ω is robust against a small external magnetic field, which is crucial to experimentally observing such coherent beating of the electron spin. When $\omega_0 \ll \Omega$,

$$\omega_i \simeq \Omega + \omega_0 \cos \theta_i, \quad (6.16)$$

and $\mathbf{n}_i \simeq \Omega/\Omega$. By following the same procedure as in the case of zero magnetic field, the time evolution of $\mathbf{M}$ is found to be described by Eq. (6.14) with Ω replaced by ω_i in Eq. (6.16). For a random variable $\cos \theta_i$ that follows a Gaussian distribution,

$$\langle e^{it\omega_0 \cos \theta_i} \rangle = e^{-\frac{1}{2} \langle t^2 \omega_0^2 \cos^2 \theta_i \rangle} = e^{-\frac{1}{6} \omega_0^2 t^2}, \quad (6.17)$$

we obtain

$$\mathbf{M}(t) = \frac{1}{3} M_0 (1 + 2 \cos \Omega t e^{-\frac{\omega_0^2}{6} t^2}) e^{-t/\tau}. \quad (6.18)$$

According to Eq. (6.18), the external magnetic field causes dephasing in the electron spin precession around local HFI fields at different sites, which reduces the spin relaxation time. If we study the decay of the envelop function in Eq. (6.18), the effective relaxation rate is

$$\frac{1}{T_1} = \frac{1}{\tau} + \frac{\omega_0^2}{6} \tau = \frac{96\bar{\eta}^2 + \omega_0^2}{24\bar{\eta}}. \quad (6.19)$$

Equation (6.19) indicates that the effective spin relaxation time decreases with increasing the external magnetic field. Conventionally, an external magnetic field increases the Zeeman splitting between the up and down spins, which impedes spin relaxation. Here we have shown that an external magnetic field may also *enhance* spin relaxation.

3. Large magnetic field, $\omega_0 > \Omega$

The coherent beating discussed above disappears as the external field becomes dominant over the HFI field,

where the electron spin mainly precess around the external field. At the strong field limit, $\omega_0 \gg \Omega$, the total local field is

$$\omega_i \simeq \omega_0 + \Omega \cos \theta_i, \quad (6.20)$$

and $\mathbf{n}_i \simeq \mathbf{e}_z$. The spin precession at the individual sites is

$$\frac{M_{ix}^0}{M_0} = \frac{\Omega}{\omega_0} [\sin \theta_i \cos \theta_i \cos \phi_i (1 - \cos \omega_i t) - \sin \theta_i \sin \phi_i \sin \omega_i t], \quad (6.21)$$

$$\frac{M_{iy}^0}{M_0} = \frac{\Omega}{\omega_0} [\sin \theta_i \cos \theta_i \sin \phi_i (1 - \cos \omega_i t) + \sin \theta_i \cos \phi_i \sin \omega_i t], \quad (6.22)$$

$$\frac{M_{iz}^0}{M_0} = 1. \quad (6.23)$$

Consequently,

$$\langle \mathbf{M}_i^0 \cdot \mathbf{M}_j^0 \rangle = M_{iz}^0 M_{jz}^0 = M_0^2, \quad (6.24)$$

$$\langle |\mathbf{M}_i^0|^2 \rangle = 1 + \frac{2\Omega^2}{3\omega_0^2}, \quad (6.25)$$

and we obtain from Eq. (6.9),

$$\mathbf{M}(t) = \frac{1}{N} \sum_i M_{iz} \mathbf{e}_z e^{-t/T_1} = \mathbf{M}(0) e^{-t/T_1}, \quad (6.26)$$

with

$$T_1^{-1} = \frac{2\Omega^2}{3\omega_0^2} \sum_j \eta_{ij} \simeq \frac{4\Omega^2}{\omega_0^2} \bar{\eta}. \quad (6.27)$$

In this case, it is clear that the spin relaxation rate is reduced by the external magnetic field, which is in contrast with the situation discussed in Sec. VI.A.2.

The high-field situation can be better understood from the spin-mixing picture introduced in studying the SOC.⁴ In the presence of HFI, the eigenstate at site i cannot be a pure spin state, but rather, a linear combination of the up- and down-spin states.

$$|i+\rangle = |i\uparrow\rangle + \frac{(\Omega_{ix} + i\Omega_{iy})}{2\omega_0} |i\downarrow\rangle, \quad (6.28)$$

$$|i-\rangle = |i\downarrow\rangle - \frac{(\Omega_{ix} - i\Omega_{iy})}{2\omega_0} |i\uparrow\rangle. \quad (6.29)$$

Thus, one can define a spin admixture in an eigenstate, which describes the percentage of down-spin (up-spin) portion in the quasi “up”-spin (“down”-spin) eigenstates $|i\pm\rangle$,

$$\chi^2 = \frac{|\Omega_{ix} + i\Omega_{iy}|^2}{4\omega_0^2} = \frac{\Omega^2}{6\omega_0^2}. \quad (6.30)$$

Any hopping between the two sites i and j will contain a small portion of the spin flip

$$\begin{aligned}\eta_{ij}^{+-} &\equiv \int_0^\infty \langle j - |H_{\text{int}}^*(t)H_{\text{int}}^*(t+\tau)|i+\rangle e^{-(E_i-E_j)\tau/\hbar} d\tau \\ &= 2\chi^2\eta_{ij}.\end{aligned}\quad (6.31)$$

Accordingly, the spin relaxation rate is

$$\frac{1}{T_1} = \sum_j (\eta_{ij}^{+-} + \eta_{ij}^{-+}) = \frac{2\Omega^2}{3\omega_0^2} \sum_j \eta_{ij} \simeq \frac{4\Omega^2}{\omega_0^2} \bar{\eta},$$

which is identical to Eq. (6.27) and indicates that the magnetic field reduces spin relaxation by suppressing spin mixing in an eigenstate.

B. Fast hopping

When the polaron hopping is fast, the electron spin precession around the local HFI field is frequently interrupted by the spin moving to a new site with the local HFI field oriented along a different direction. In this case the HFI-induced spin precession can be treated as a perturbation with respect to the polaron hopping among different sites. In the absence of the HFI, it is readily seen from Eq. (5.12) that a fast hopping leads to the equilibrium of the system with spin polarization $\mathbf{M}_i = \mathbf{M}$ uniform throughout the system.

1. Zero magnetic field $\omega_0 = 0$

When the HFI is turned on, the local spin polarization slightly deviates from the uniform magnetization $\mathbf{M}$ and can be expressed as

$$\mathbf{M}_i = \mathbf{M} + \delta\mathbf{M}_i. \quad (6.32)$$

Since in this regime spin precession around the local HFI field is frequently interrupted, $\delta\mathbf{M}_i$ is small. Keeping the lowest order of $\delta\mathbf{M}_i$, we obtain

$$\frac{d\mathbf{M}}{dt} = \mathbf{M} \times \boldsymbol{\Omega}_i - \sum_j \eta_{ij} (\delta\mathbf{M}_i - \delta\mathbf{M}_j) + \delta\mathbf{M}_i \times \boldsymbol{\Omega}_i, \quad (6.33)$$

We have dropped the term, $\frac{d\delta\mathbf{M}_i}{dt}$, for we are concerned with the relaxation of the overall magnetization $\mathbf{M}$ and the ensemble average of $\frac{d\delta\mathbf{M}_i}{dt}$ must cancel out. Since η_{ij} is much faster than Ω_i , we search for a solution in the form,

$$\delta\mathbf{M}_i = \int d\tau e^{-\tau/\tau_c} \mathbf{M} \times \boldsymbol{\Omega}_i(0) = \tau_c \mathbf{M} \times \boldsymbol{\Omega}_i(0), \quad (6.34)$$

in which the time scale τ_c is chosen to satisfy

$$\mathbf{M} \times \boldsymbol{\Omega}_i - \sum_j \eta_{ij} (\delta\mathbf{M}_i - \delta\mathbf{M}_j) = 0. \quad (6.35)$$

Here τ_c measures the average time an electron spin precesses around the local magnetic field, $\boldsymbol{\Omega}_i$, before it is interrupted by polaron hopping to another site. The physics is that because of the rapid hopping, an electron spin fluctuation $\delta\mathbf{M}_i$ (developed due to the local HFI field) is quickly balanced by its fast hopping. This quasi-balance assumption allows us to eliminate the fast hopping process. This approach follows the same spirit as in the classic work by D'yakonov and Perel' on spin relaxation in semiconductors.²⁹ If $\delta\mathbf{M}_i$ and $\delta\mathbf{M}_j$ are uncorrelated, Eqs. (6.34) and (6.35) yield

$$\tau_c^{-1} = \sum_j \eta_{ij} \simeq 6\bar{\eta}. \quad (6.36)$$

Substituting Eqs. (6.34) and (6.35) into Eq. (6.33), we have

$$\frac{d\mathbf{M}}{dt} = - \int_0^\infty d\tau e^{-\tau/\tau_c} \langle [\mathbf{M} \times \boldsymbol{\Omega}_i(0)] \times \boldsymbol{\Omega}_i(\tau) \rangle, \quad (6.37)$$

or equivalently,

$$\frac{d\mathbf{M}}{dt} = -\tau_c \mathbf{M} \langle \boldsymbol{\Omega}_{i\perp} \cdot \boldsymbol{\Omega}_{i\perp} \rangle \equiv \tau_c \mathbf{M} \langle \Omega_{ix}^2 + \Omega_{iy}^2 \rangle. \quad (6.38)$$

Here $\boldsymbol{\Omega}_{i\perp}$ is the transverse component of the local HFI field with respect to $\mathbf{M}$ and $\boldsymbol{\Omega}_i(t)$ is independent of time. The spin relaxation rate is therefore

$$\frac{1}{T_1} = \tau_c \langle \Omega_{ix}^2 + \Omega_{iy}^2 \rangle = \frac{2}{3} \Omega^2 \tau_c \simeq \frac{\Omega^2}{9\bar{\eta}}. \quad (6.39)$$

Equation (6.39) indicates that in the fast-hopping regime, polaron hopping *inhibits* electron spin relaxation because the fast polaron hopping reduces the time for electron spin precession around the local HFI field. This behavior can be understood in terms of the random walk analogy: The spin relaxation T_1 is roughly the time needed for the electron spin to change its orientation by 1 radian. Between any consecutive two hops, the precession angle around the local HFI field is about $\Omega\tau_c$. Since the local HFI fields at different sites are randomly oriented, the electron spin precession angle $\Delta\varphi$ after n hops is about $(\Delta\varphi)^2 = n(\Omega\tau_c)^2$. By requiring $(\Delta\varphi)^2 \sim 1$ when $n \sim T_1/\tau_c$, we have $1/T_1 \sim \Omega^2\tau_c$. Equations (6.19) and (6.39) succinctly illustrates the opposite effects of $\bar{\eta}$ on spin relaxation in different regimes.

2. Finite magnetic field

In the presence of a finite magnetic field ω_0 , we can work in a coordinate frame rotating around the z -axis at frequency ω_0 , in which the external magnetic field is removed. In the rotating frame, the local HFI field becomes time dependent,

$$\tilde{\Omega}_{ix}(t) = \Omega_{ix} \cos \omega_0 t + \Omega_{iy} \sin \omega_0 t, \quad (6.40)$$

$$\tilde{\Omega}_{iy}(t) = -\Omega_{ix} \sin \omega_0 t + \Omega_{iy} \cos \omega_0 t, \quad (6.41)$$

$$\tilde{\Omega}_{iz}(t) = \Omega_{iz}. \quad (6.42)$$

Following the same strategy as in the above section, the local fluctuation $\delta\mathbf{M}_i$ can be written as

$$\delta\mathbf{M}_i = \int_0^\infty d\tau e^{-\tau/\tau_c} \mathbf{M} \times \tilde{\Omega}_i(0), \quad (6.43)$$

and the spin relaxation is

$$\begin{aligned} \frac{d\mathbf{M}}{dt} &= \int_0^\infty d\tau e^{-\tau/\tau_c} \langle [\mathbf{M} \times \tilde{\Omega}_i(0)] \times \tilde{\Omega}_i(\tau) \rangle \\ &= \int_0^\infty d\tau e^{-\tau/\tau_c} \mathbf{M} \langle \tilde{\Omega}_{ix}(0) \tilde{\Omega}_{ix}(\tau) \\ &\quad + \tilde{\Omega}_{iy}(0) \tilde{\Omega}_{iy}(\tau) \rangle. \end{aligned} \quad (6.44)$$

Substituting Eqs. (6.40)-(6.42) into Eq. (6.44), we obtain the spin relaxation rate,

$$\begin{aligned} \frac{1}{T_1} &= \langle \Omega_{ix}^2 + \Omega_{iy}^2 \rangle \frac{\tau_c}{1 + \omega_0^2 \tau_c^2} \\ &= \frac{2\Omega^2 \tau_c}{3(1 + \omega_0^2 \tau_c^2)} = \frac{4\Omega^2 \bar{\eta}}{36\bar{\eta}^2 + \omega_0^2}. \end{aligned} \quad (6.45)$$

Equation (6.45) suggests that in the fast-hopping regime, the magnetic field ω_0 always suppresses spin relaxation. This is reasonable because in the presence of a strong magnetic field, electron spin precession around the external field becomes significant, which suppresses the spin precession along the HFI field.

C. Fluctuating field approach

In the fast hopping regime, the hopping process can be characterized by a correlation time, $\tau_c \simeq 1/6\bar{\eta}$, beyond which electron spin can be regarded as being at a different location with the local HFI field oriented along another direction. Thus, spin relaxation can be studied by assuming that the HFI field experienced by an electron spin varies temporally with a correlation time τ_c . The coupling between the electron spin and the fluctuating HFI field is

$$\begin{aligned} V(t) &= \sum_{\alpha} [\hat{\mathbf{S}} \cdot \mathbf{T}^{\alpha}(t) \cdot \mathbf{I}_{\alpha}(t) + A_{\alpha} \hat{\mathbf{S}} \cdot \mathbf{I}_{\alpha}(t)] \\ &= \hbar \gamma \hat{\mathbf{S}} \cdot \mathbf{B}_H(t), \end{aligned} \quad (6.46)$$

with

$$\overline{\mathbf{B}_H(t) \mathbf{B}_H(t + \tau)} = B_H^2 e^{-|\tau|/\tau_c}. \quad (6.47)$$

Spin relaxation in the presence of a fluctuating magnetic field has been obtained from the Redfield theory, and the relaxation rate is¹⁴

$$\frac{1}{T_1} = \gamma^2 \frac{\tau_c}{1 + \omega_0^2 \tau_c^2} (\langle |B_{Hx}|^2 \rangle + \langle |B_{Hy}|^2 \rangle). \quad (6.48)$$

Substituting Eq. (6.46) into Eq. (6.48), we have

$$\frac{1}{T_1} = \frac{1}{\hbar^2} \frac{\tau_c}{1 + \omega_0^2 \tau_c^2} \sum_{\alpha} \langle A_{\alpha}^2 (I_{\alpha x}^2 + I_{\alpha y}^2) + I_{\alpha x}^2 [(T_{xx}^{\alpha})^2 + (T_{yx}^{\alpha})^2] + I_{\alpha y}^2 [(T_{xy}^{\alpha})^2 + (T_{yy}^{\alpha})^2] + I_{\alpha z}^2 [(T_{xz}^{\alpha})^2 + (T_{yz}^{\alpha})^2] \rangle. \quad (6.49)$$

Since $\mathbf{T}^{\alpha} : \mathbf{T}^{\alpha}$ is rotational invariant,

$$\begin{aligned} \langle T_{zx}^{\alpha} T_{zx}^{\alpha} \rangle &= \frac{1}{6} (\mathbf{T}^{\alpha} : \mathbf{T}^{\alpha}) \langle 9 \cos^2 \theta_{\alpha} \sin^2 \theta_{\alpha} \cos^2 \phi_{\alpha} \rangle \\ &= \frac{1}{10} (\mathbf{T}^{\alpha} : \mathbf{T}^{\alpha}), \end{aligned} \quad (6.50)$$

and similarly,

$$\begin{aligned} \langle T_{zy}^{\alpha} T_{zy}^{\alpha} \rangle &= \frac{1}{10} (\mathbf{T}^{\alpha} : \mathbf{T}^{\alpha}), \\ \langle T_{xx}^{\alpha} T_{xx}^{\alpha} \rangle &= \frac{2}{15} (\mathbf{T}^{\alpha} : \mathbf{T}^{\alpha}), \end{aligned} \quad (6.51)$$

Equation (6.49) reduces to

$$\frac{1}{T_1} = \gamma^2 \frac{\tau_c}{1 + \omega_0^2 \tau_c^2} \frac{2}{3} (B_I^2 + B_D^2) = \frac{\Omega^2}{3} J(\omega_0), \quad (6.52)$$

where

$$J(\omega) \equiv \int_{-\infty}^{+\infty} d\tau e^{i\omega\tau} e^{-|\tau|/\tau_c} = \frac{2\tau_c}{1 + \omega^2 \tau_c^2}. \quad (6.53)$$

This is the same as Eq. (6.45).

D. Quantum treatment

The HFI effect on spin relaxation has so far been treated within a classical picture, in a sense that the nuclear spin is considered as a static magnetic field. In this subsection, we show the results remain unchanged if the HFI is treated quantum mechanically. We will use fast hopping as an example, where the polaron hopping is described by a correlation time between the HFI fields. The unperturbed Hamiltonian is the Zeeman energy of the electron spin (the Zeeman energy of the nuclear spin is neglected),

$$H_0 = \hbar \omega_0 \hat{S}_z, \quad (6.54)$$

and the interaction is

$$H_{\text{int}} \equiv H_I + H_D = \sum_{\alpha} (A_{\alpha} \hat{\mathbf{I}}_{\alpha} \cdot \hat{\mathbf{S}} + \hat{\mathbf{I}}_{\alpha} \cdot \mathbf{T}^{\alpha} \cdot \hat{\mathbf{S}}). \quad (6.55)$$

The electron spin relaxation can be studied by solving the Redfield equation in the interaction representation,

$$\frac{d\hat{\rho}^*}{dt} = -\frac{1}{\hbar^2} \int_0^\infty d\tau \overline{[H_{\text{int}}^*(t), [H_{\text{int}}^*(t+\tau), \hat{\rho}^*(0)]]},$$

where $\hat{\rho}$ is the electron density matrix, which is homogeneous across the system.

$$\begin{aligned} H_I^*(t) &\equiv e^{iH_0 t/\hbar} H_I e^{-iH_0 t/\hbar} \\ &= \sum_{\alpha} A_{\alpha} \left[\hat{I}_{\alpha z} \hat{S}_z \right. \\ &\quad \left. + \frac{1}{2} (\hat{I}_{\alpha+} \hat{S}_- e^{-i\omega_0 t} + \hat{I}_{\alpha-} \hat{S}_+ e^{i\omega_0 t}) \right], \end{aligned} \quad (6.56)$$

$$\begin{aligned} H_D^*(t) &\equiv e^{iH_0 t/\hbar} H_D e^{-iH_0 t/\hbar} \\ &= \hbar^2 \gamma \sum_{\alpha} \gamma_N^{\alpha} \left[F_{\alpha}^{(0)} \left(\hat{I}_{\alpha z} \hat{S}_z \right. \right. \\ &\quad \left. \left. - \frac{1}{4} (\hat{I}_{\alpha+} \hat{S}_- e^{-i\omega_0 t} + \text{H.c.}) \right) \right. \\ &\quad \left. - \frac{3}{2} F_{\alpha}^{(1)} \left(\hat{I}_{\alpha+} \hat{S}_z + \hat{I}_{\alpha z} \hat{S}_+ e^{i\omega_0 t} + \text{H.c.} \right) \right. \\ &\quad \left. + \frac{3}{4} F_{\alpha}^{(2)} \left(\hat{I}_{\alpha+} \hat{S}_+ e^{i\omega_0 t} + \text{H.c.} \right) \right]. \end{aligned} \quad (6.57)$$

Since the local HFI field at a molecule is randomly oriented, the average, $\langle \hat{I}_{\alpha} \rangle$, over a large system is zero. Taking the trace of $\hat{S}_z \hat{\rho}^*$, we obtain

$$\frac{d\langle \hat{S}_z \rangle}{dt} \equiv \frac{d}{dt} \text{Tr} \hat{S}_z \hat{\rho}^* = \text{Tr} \hat{S}_z \dot{\hat{\rho}}^*, \quad (6.58)$$

where

$$\hat{S}_z = \frac{1}{\hbar^2} \int_0^\infty d\tau \overline{[H_{\text{int}}^*(t), [H_{\text{int}}^*(t+\tau), \hat{S}_z]]}. \quad (6.59)$$

The spin relaxation time can be obtained by expressing the right-hand side of Eq. (6.59) as

$$\text{Tr} \hat{S}_z \dot{\hat{\rho}}^* = -\frac{1}{T_1} \langle \hat{S}_z \rangle. \quad (6.60)$$

$\hat{S}_z$ due to the isotropic term H_I^* is

$$\begin{aligned} \hat{S}_z^I &= -\frac{1}{2\hbar^2} \int_0^{+\infty} d\tau \sum_{\alpha} A_{\alpha}^2 \left[\overline{\langle \hat{I}_{\alpha+}(t) \hat{I}_{\alpha'-}(t+\tau) \rangle} e^{-i\omega_0 \tau} \right. \\ &\quad \left. + \overline{\langle \hat{I}_{\alpha-}(t) \hat{I}_{\alpha'+}(t+\tau) \rangle} e^{i\omega_0 \tau} \right] \hat{S}_z \\ &= \frac{A_{\alpha}^2}{3\hbar^2} J(\omega_0) \hat{S}_z, \end{aligned} \quad (6.61)$$

where we have assumed the temporal correlation

$$\overline{\hat{I}_{\alpha+}(t) \hat{I}_{\alpha-}(t+\tau)} = \hat{I}_{\alpha+} \hat{I}_{\alpha-} e^{-|\tau|/\tau_c}. \quad (6.62)$$

and used the relation for the ensemble average

$$\langle \hat{I}_{\alpha+} \hat{I}_{\alpha'-} \rangle = \langle \hat{I}_{\alpha+} \hat{I}_{\alpha-} \rangle \delta_{\alpha\alpha'} = \frac{2}{3} \delta_{\alpha\alpha'} I_{\alpha} (I_{\alpha} + 1). \quad (6.63)$$

Thus, the spin relaxation rate due to the isotropic HFI is

$$\frac{1}{T_{1I}} = \frac{\gamma^2 B_I^2}{3} J(\omega_0), \quad (6.64)$$

which is the expression obtained in Ref. 11.

$\hat{S}_z$ due to the dipolar interaction H_D^* from evaluating Eq. (6.59) is

$$\begin{aligned} \hat{S}_z^D &= \frac{1}{\hbar^2} \sum_{\alpha} \left[\frac{J^{(0)}(\omega_0)}{4} + \frac{9J^{(1)}(\omega_0)}{2} + \frac{9J^{(2)}(\omega_0)}{4} \right] \\ &\quad \times \langle \hat{I}_{\alpha+} \hat{I}_{\alpha-} \rangle \hat{S}_z, \end{aligned} \quad (6.65)$$

where

$$J^{(q)}(\omega) = (\hbar \gamma \gamma_N^{\alpha})^2 \int_{-\infty}^{\infty} \overline{F^{(q)}(t) F^{(q)*}(t+\tau)} e^{-i\omega \tau} d\tau. \quad (6.66)$$

By using Eq. (6.60), the spin relaxation rate due to the dipolar coupling can be expressed as

$$\begin{aligned} \frac{1}{T_{1D}} &= \sum_{\alpha} I_{\alpha} (I_{\alpha} + 1) \left[\frac{J^{(0)}(\omega_0)}{12} \right. \\ &\quad \left. + \frac{3}{2} J^{(1)}(\omega_0) + \frac{3}{4} J^{(2)}(\omega_0) \right]. \end{aligned} \quad (6.67)$$

The value of $J^{(0)}(\omega)$ is

$$\begin{aligned} J^{(0)}(\omega) &= \frac{2\tau_c}{1 + \omega^2 \tau_c^2} (\hbar \gamma \gamma_N^{\alpha})^2 \left\langle \left(\frac{1 - 3 \cos^2 \theta_{\alpha}}{|\mathbf{r} - \mathbf{r}_{\alpha}|} \right)^2 \right\rangle \\ &= \frac{2\tau_c}{1 + \omega^2 \tau_c^2} \frac{4}{5} (\hbar \gamma \gamma_N^{\alpha})^2 \left\langle \frac{1}{r^6} \right\rangle \\ &= J(\omega) \sum_{\alpha} \frac{2}{15\hbar^2} \mathbf{T}^{\alpha} : \mathbf{T}^{\alpha}. \end{aligned} \quad (6.68)$$

Similarly,

$$J^{(1)}(\omega) = \frac{1}{45\hbar^2} J(\omega) \sum_{\alpha} \mathbf{T}^{\alpha} : \mathbf{T}^{\alpha}, \quad (6.69)$$

$$J^{(2)}(\omega) = \frac{4}{45\hbar^2} J(\omega) \sum_{\alpha} \mathbf{T}^{\alpha} : \mathbf{T}^{\alpha}. \quad (6.70)$$

Thus, the spin relaxation rate due to the dipolar HFI is

$$\frac{1}{T_{1D}} = \frac{\gamma^2 B_D^2}{3} J(\omega_0). \quad (6.71)$$

The total spin relaxation rate with both the isotropic and dipolar contributions included is

$$\frac{1}{T_1} = \frac{1}{T_{1I}} + \frac{1}{T_{1D}} = \frac{\gamma^2 B_H^2}{3} J(\omega_0) \equiv \frac{\Omega^2}{3} J(\omega_0), \quad (6.72)$$

which is identical to Eqs. (6.45) and (6.52) obtained by treating the HFI classically. Therefore, both the classical and quantum theories indicate that the spin relaxation time is directly related to the effective magnetic field, B_H , defined in Eq. (2.9).

E. General cases

When the hopping rate $\bar{\eta}$ and Larmor frequency Ω of the HFI are comparable, the compact expressions obtained in the limiting cases above become inaccurate. We numerically solve the obtained time-dependent master equation with the initial condition being a uniform spin polarization. Figure 2 shows the time evolution of the macroscopic spin polarization $\mathbf{M}$ in different regimes. In the slow hopping regime ($\bar{\eta} \ll \Omega$), when the external magnetic field is small, $\omega_0 \ll \Omega$, a coherent beating of total spin polarization at frequency Ω is present, as shown in the left panel of Fig. 2. A small external field ω_0 causes dephasing of the beating and makes the effective relaxation time shorter. As ω_0 increases, the coherent beating is visible only at the initial stage as illustrated by the black line in the right panel of Fig. 2. In the fast hopping regime, the beating disappears and $\mathbf{M}$ exhibits an exponential decay over time, from which a relaxation time can be readily extracted.

The spin relaxation time T_1 from our numerical results is plotted in Fig. 3 as a function of the external field ω_0 and the hopping rate $\bar{\eta}$. When $\bar{\eta} \ll \Omega$, as illustrated by the black curve, the spin relaxation time T_1 first decreases and then increases with ω_0 . The numerical results coincide with that from Eq. (6.19) at weak magnetic fields, and agree with that from Eq. (6.27) at strong fields. The excellent agreement between the numerical results and the analytical expressions indicate: (i) that the theories capture major physics and, (ii) that the numerical results are reliable. The initial decrease in T_1 versus ω_0 is due to the magnetic field-induced dephasing among coherent precession of individual electron spins at different sites. This is a rare example that an external magnetic field can enhance the electron spin relaxation. The increase in T_1 with ω_0 when $\omega_0 > \Omega$ is due to the fact that the HFI-induced spin mixing in an eigenstate becomes smaller as ω_0 increases.

In the fast hopping regime, as delineated by the gray lines in Fig. 3, the spin relaxation time T_1 increases slightly versus the magnetic field ω_0 until ω_0 becomes comparable to the hopping rate $\bar{\eta}$. In this case a spin precession is frequently interrupted by the fast polaron hopping to adjacent sites whose HFI fields orient along different directions. The average polaron dwell time at a given site is $\tau_c \simeq (6\bar{\eta})^{-1}$, during which the precession around the external field, $\omega_0\tau_c$, is negligible for small ω_0 . Consequently the spin precession is still around the randomly oriented HFI field, and therefore the spin relaxation time depends only weakly on ω_0 . When the magnetic field is strong, $\omega_0\tau_c > 1$, the precession around the external field becomes significant, which suppresses the spin precession along the HFI field as well as the spin relaxation. In this case the spin relaxation time increases with the magnetic field rapidly, proportional to ω_0^2 .

Figure 3 also plots the spin relaxation time T_1 as a function of the hopping rate $\bar{\eta}$ under different external fields. The spin relaxation time T_1 initially decreases and

then increases with $\bar{\eta}$. In other words, when $\bar{\eta} \ll \Omega$, the electron hopping induces spin relaxation, whereas $\bar{\eta} \gg \Omega$, the hopping inhibits spin relaxation. According to Fig. 3, when the external field ω_0 is very small, crossover takes place when the hopping rate $1/\tau_c \simeq 6\bar{\eta}$ is comparable to Ω . When the external field is strong, the crossover takes place at $1/\tau_c \sim \omega_0$. The numerical results again show an excellent agreement with the analytical expressions of Eqs. (6.18) and (6.26) at the slow hopping regime as well as Eq. (6.44) at the fast-hopping regime.

It should be noted that Eq. (6.45) is obtained in the fast-hopping regime and may not be valid when the hopping rate $\bar{\eta}$ is small. Indeed, Eq. (6.45) shows significant deviation from the numerical results when $\bar{\eta}$ is small and the magnetic field is weak. While earlier studies considered only the fast-hopping regime,¹¹ Eq. (6.45) was usually assumed to be general. However, a very small magnetic field in Eq. (6.45) would predict a monotonic dependence on the hopping rate, which is physically incorrect. We emphasize that even at zero external field, the spin relaxation time T_1 increases as the hopping rate diminishes.

The hopping rate in organics generally exhibits a thermally activated behavior,

$$\bar{\eta} = \eta_0 e^{-E/k_B T}, \quad (6.73)$$

where E is the energy barrier. Thus, by changing the temperature, the hopping rate may vary significantly. The magnetic field and hopping dependences of the spin relaxation time illustrated in Fig. 3 can be used to identify dominant mechanisms of the spin relaxation in individual organics, via the SOC or HFI. When spin relaxation is caused by the SOC, as pointed out in Ref. 4, the spin relaxation time T_1 would be independent of the external magnetic field and decrease with the hopping rate (temperature). To date, very few systematic studies have been carried out on the magnetic field and temperature dependences of the spin relaxation time. The only study that the authors are aware of is the temperature-dependent spin relaxation in Alq₃ and related materials at large magnetic fields up to 1.5 T,³⁰ where, according to Eqs. (6.27) and (6.45), the HFI-induced spin relaxation becomes negligible. This study indicates a monotonic increase in spin relaxation time with temperature, supporting a SOC mechanism of spin relaxation.

VII. SPIN DIFFUSION

When discussing spin relaxation we have considered the time evolution of the average magnetization of the whole system. To study spin diffusion, the initial system must have inhomogeneous spin polarization so that diffusion can take place. The inhomogeneous spin polarization is present in the spin-injection structures such as spin valves.^{1,2}

FIG. 2: (Color online) Time evolution of the average electron spin, with $\mathbf{M}_i(t=0) = \mathbf{e}_z$, by numerically solving time-dependent master equations. In the left panel, light gray (green) and dark gray (blue) lines correspond to $(\omega_0/\Omega, \bar{\eta}/\Omega) = (0.01, 0.01)$ and $(0.25, 0.01)$. In the right panel, dark (black) and gray (red) lines correspond to $(\omega_0/\Omega, \bar{\eta}/\Omega) = (3.98, 0.01)$ and $(0.01, 1.58)$. The amplitude of HFI field is fixed at 1 mT or $\Omega = 1.8 \times 10^8$ Hz.

FIG. 3: (Color online) Spin relaxation time T_1 as a function of external magnetic field (left panel) and polaron hopping rate (right panel) by solving the master equations in a $32 \times 32 \times 32$ lattice. Dark (black) and gray (red) solid lines correspond to $\eta/\Omega = 0.01$ and 10. Dashed, dot-dashed and dotted lines are obtained from Eqs. (6.19), (6.27), and (6.45), respectively. In the right panel, dark (black) and gray (red) solid lines correspond to $\omega_0/\Omega = 0.1$ and 10. The amplitude of the HFI field is fixed at 1 mT.

A. Slow hopping

In the slow-hopping regime, when the external field is much smaller than the HFI, the electron spin precesses around the local HFI. The slow varying spin polarization is projected along the local HFI axis. When the electron hops to adjacent sites, its spin will orient along different directions. Thus, the spin diffusion length is shorter than

the inter-molecular distance.

When a global spin polarization is well defined, namely $\omega_0 \gg \Omega$, the time-independent spin polarization at each site, according to Eqs. (6.21)-(6.23) is

$$\bar{\mathbf{M}}_i = \bar{M}_i \left(\frac{\Omega}{\omega_0} \sin \theta_i \cos \phi_i, \frac{\Omega}{\omega_0} \sin \theta_i \sin \phi_i, 1 \right) \simeq \bar{M}_i \mathbf{e}_z. \quad (7.1)$$

We seek to derive a steady-state equation for $\bar{\mathbf{M}}_i$. Since the introduction of hopping causes a decay of spin polarization over time,

$$\mathbf{M}_i = A \bar{\mathbf{M}}_i = \bar{\mathbf{M}}_i e^{-t/\tau}, \quad (7.2)$$

and from Eqs. (6.7) and (6.27), we obtain the static equation

$$\sum_j \eta_{ij} \frac{2\Omega^2}{3\omega_0} \bar{\mathbf{M}}_i - \sum_j \eta_{ij} (\bar{\mathbf{M}}_i - \bar{\mathbf{M}}_j) = 0. \quad (7.3)$$

By comparing Eq. (7.3) to Eq. (5.18), the spin diffusion length is obtained,

$$L_s = \frac{\omega_0}{2\Omega} a. \quad (7.4)$$

This result can also be obtained by examining the spin mixing induced by the HFI. The spin diffusion due to the SOC was analyzed in terms of spin mixing and found to satisfy the following difference equation,⁴

$$0 = \sum_j \eta_{ij} [(1 - 2\chi^2) \bar{\mathbf{M}}_j - (1 + 2\chi^2) \bar{\mathbf{M}}_i], \quad (7.5)$$

where χ^2 is the spin admixture between the up and down spin states in an eigenstate caused by the SOC. The obtained equation in Ref. 4 can be used in this situation as well, by replacing χ^2 there with the spin mixing caused by the HFI, $\chi^2 = \Omega^2/6\omega_0^2$. The spin diffusion length L_s is

$$L_s = \sqrt{\frac{1}{24\chi^2}} a = \frac{\omega_0}{2\Omega} a,$$

which is identical to Eq. (7.4). We see that the spin diffusion length in the slow-hopping regime is independent of the hopping rate $\bar{\eta}$ but increases linearly with the magnetic field ω_0 . The $\bar{\eta}$ independence is caused by the two opposite effects of $\bar{\eta}$: On the one hand, it gives rise to spin relaxation as in Eq. (6.27) and makes spin diffusion length shorter; On the other hand, it enables electron spins to migrate. The ω_0 dependence is due to the suppression of spin mixing by the external field.

B. Fast hopping

In the fast-hopping regime, the steady-state master equation can be written in the rotating frame as

$$0 = (\bar{\mathbf{M}}_i + \delta \mathbf{M}_i) \times \tilde{\Omega}_i - \sum_j \eta_{ij} (\bar{\mathbf{M}}_i - \bar{\mathbf{M}}_j) - \sum_j \eta_{ij} (\delta \mathbf{M}_i - \delta \mathbf{M}_j). \quad (7.6)$$

Since the spin polarization direction in a device structure is determined by the spin polarization at the boundaries, $\bar{\mathbf{M}}_i$'s at different sites are along the same direction, say the z -axis. Following the same argument as in Sec. VI.B, we express $\delta\mathbf{M}_i$ as

$$\delta\mathbf{M}_i = \int_0^\infty d\tau e^{-\tau/\tau_c} \bar{\mathbf{M}}_i \times \tilde{\mathbf{\Omega}}_i, \quad (7.7)$$

so that

$$\frac{\delta\mathbf{M}_i}{\tau_c} - \sum_j \eta_{ij} (\delta\mathbf{M}_i - \delta\mathbf{M}_j) = 0, \quad (7.8)$$

and Eq. (7.6) reduces to

$$0 = \bar{\mathbf{M}}_i \cdot \int_0^\infty d\tau e^{-\tau/\tau_c} [\tilde{\mathbf{\Omega}}_{i\perp}(0) \cdot \tilde{\mathbf{\Omega}}_{i\perp}(\tau)] - \sum_j \eta_{ij} (\bar{\mathbf{M}}_i - \bar{\mathbf{M}}_j). \quad (7.9)$$

Comparing Eq. (7.9) with (5.18) and using Eq. (6.45), we obtain the spin diffusion length

$$L_s = \frac{a}{2\Omega} \sqrt{36\bar{\eta}^2 + \omega_0^2}. \quad (7.10)$$

When the external field is zero, it reduces to

$$L_s = \frac{3a}{\Omega} \bar{\eta}, \quad (7.11)$$

which increases linearly with the hopping rate $\bar{\eta}$. We would like to point out that Eq. (7.10) was derived in the fast-hopping regime and may be invalid in the slow-hopping regime. Under large external magnetic fields with $\omega_0 \gg \bar{\eta}$, the expression is

$$L_s = \frac{\omega_0}{2\Omega} a. \quad (7.12)$$

This is the same as Eq. (6.15) obtained in the slow-hopping regime. The reason of this agreement is that when ω_0 is the shortest time scale, both the HFI field and hopping are perturbations.

C. General case

In general situations, we can numerically solve the original steady state master equation Eq. (5.12) with proper boundary conditions. Since the steady-state equations are linear, in principle the exact solution can be obtained.

We consider a $32 \times 32 \times 32$ cubic lattice with the HFI field $\mathbf{\Omega}_i$ on any site oriented along an arbitrary direction. An external field ω_0/γ is applied along the z -axis. The boundary condition is set as follows. In the plane of $l = 1$ spin polarization is set zero, $\mathbf{M}(l = 1, m, n) = 0$, and in the plane of $l = 32$, it is set to be $\mathbf{M}(l = 32, m, n) = M_0 \mathbf{e}_z$. Then, we numerically solve the $3 \times 32 \times 32 \times 30$ unknowns, $\mathbf{M}(l, m, n)$ for site $1 \leq m, n \leq 32$, $2 \leq l \leq 31$ using the sparse-matrix techniques because electron

hopping takes place only between adjacent sites. We plot in Fig. 4 the averaged $\bar{M}_z(l)$ in each plane,

$$\bar{M}_z(l) = \frac{1}{32 \times 32} \sum_{m,n=1}^{32} M_z(l, m, n). \quad (7.13)$$

We see that $\bar{M}_z(l)$ decays exponentially over the distance, $\bar{M}_z(l) \simeq M_0 e^{(l-32)a/L_s}$, which allows one to extract the spin diffusion length unambiguously. When the diffusion length L_s is comparable to the system size, the finite size effect becomes important and the distance dependence deviates from the exponential function, as shown in Fig. 4. In our calculations, we ensure that the system size is much larger than the diffusion length to avoid possible finite-size effect.

Figure 4 also compares the numerical results for the case of $\omega_0 = 0$ with the analytical expression Eq. (7.11) where a fast hopping is assumed. When hopping is large, the two approaches give the same result, validating the accuracy of the numerical results. As the hopping becomes slower, the expression in Eq. (7.11) deviates from the numerically exact solution and considerably underestimates the spin diffusion length.

In Fig. 5, we plot the spin diffusion length L_s as a function of the magnetic field ω_0 and the hopping rate $\bar{\eta}$. The dashed lines are obtained from Eq. (7.10). As the external field increases, as shown in the left panel, the spin diffusion length is initially insensitive to ω_0 then increases with ω_0 quickly. The crossover takes places when $\omega_0 \sim 6\bar{\eta} = \tau_c^{-1}$, below (above) which the electron spin mainly precesses around the HFI (external) field. At high magnetic fields, all lines for different hopping rates merge into a single line, indicating that the spin diffusion length is independent of the hopping. In fact, the high-field region can be well described by Eq. (7.12), which does not depend on $\bar{\eta}$.

From the spin diffusion length L_s versus the hopping $\bar{\eta}$, we also see a crossover: L_s is insensitive to $\bar{\eta}$ when $\bar{\eta}$ is small and then increases with $\bar{\eta}$. For fast hopping the dependence can be well described by Eq. (7.10). Again, this crossover originates from the disparate spin relaxation behaviors at slow and fast hopping regimes discussed in Sec. VI. Comparing the numerical results with Eq. (7.10), the deviation occurs at small hopping and weak magnetic field regimes. In general, for weak magnetic fields Eq. (7.10) overestimates the diffusion length when the hopping rate is large but underestimates the diffusion length when hopping is small.

Figure 5 indicates that the spin diffusion length due to the HFI would increase linearly with the magnetic field ω_0 when $\omega_0 > \Omega$ and hopping $\bar{\eta}$ when $\bar{\eta} > \Omega$ [which depends on the temperature according Eq. (6.73)]. These dependences are very different from those in the SOC-induced spin diffusion, where the spin diffusion length is independent of the magnetic field and has a much weaker dependence on temperature or hopping rate. The temperature dependence of spin diffusion is studied only in Alq₃,³¹ which is consistent with the SOC mechanism.⁴

FIG. 4: (Color online) Spatial distribution of spin polarization on a $32 \times 32 \times 32$ lattice in the absence of external magnetic field. Black, dark gray (red), and light gray (green) lines correspond to $\bar{\eta}/\Omega = 0.84, 1.68$, and 5.31 . The right panel compares between the analytical solution of Eq. (7.11), depicted by the dark (black) line, and the numerical results, depicted by the gray (red) line, for $\omega_0 = 0$.

FIG. 5: (Color online) Spin diffusion length L_s as a function of external magnetic field and polaron hopping rate from numerically solving the master equations. In the left panel, black, dark gray (red), and light gray (green) lines correspond to $\bar{\eta}/\Omega = 0.063, 0.63$, and 6.3 . In the right panel, black and red lines correspond to $\omega_0/\Omega = 0.1$ and 10 . Dashed lines are from Eq. (7.10). The amplitude of the HFI field is fixed at 1 mT.

VIII. CONCLUSIONS

In this paper, we have systematically quantified the HFI strength in common organics encountered in the field of organic spintronics, and analyzed its role in the spin relaxation and diffusion in organic solids. The HFI can be described by an effective magnetic field, with contributions from both the contact and dipolar interactions. The calculated effective HFI field in all these organics are

found to be smaller than 2 mT, except in CuPc where the HFI originates from the $3d$ electrons in the Cu ion. These values are consistent with the experimental data in the ESR and NMR literature, but considerably smaller than the obtained values via the model fitting in recent studies of magnetic-field effects in organic devices. The dipolar HFI is significant and may dominate over the contact contribution in materials with weak HFIs such as C_{60} and its derivatives. The molecular geometry may affect the HFI strength. However, the impact of geometry to the HFI is much weaker than that to the SOC.

In many organics, such as Alq_3 , there exist nuclear spins other than H, which contribute to the total HFI. Deuteration effect on the HFI in these materials may be much weaker than in organics with H being the sole HFI source. We have calculated the expected deuteration effect on the HFI in common organics. These results can help interpret the deuteration experiments more reliably.

Spin relaxation and diffusion due to the HFI have been comprehensively studied. We have clarified the meaning of spin relaxation and diffusion in disordered organics and pertinent experiments to measure them. A transport equation for electron spin polarization is derived in a disordered system, where each molecule has a randomly oriented HFI field and electron conduction is via hopping among adjacent molecules. In limiting cases, when analytical solutions are possible, we have obtained compact expressions, usually with more than one approaches to ensure their correctness. For general cases we numerically solve the obtained transport equation in a 3D cubic lattice. The numerical results have been examined to reproduce the analytical results in the limiting cases, as they should.

We have found that the interplay between the electron hopping rate $\bar{\eta}$ and the electron spin precession frequency Ω around the HFI field may result in disparate spin relaxation behaviors. When $\bar{\eta} \ll \Omega$ spin relaxation rate increases with $\bar{\eta}$. On the other hand, when $\bar{\eta} \gg \Omega$ the relaxation rate decreases with $\bar{\eta}$. The diffusion length is essentially independent of $\bar{\eta}$ in the slow-hopping regime (when the magnetic field is larger than the HFI) and increases linearly with $\bar{\eta}$ in the fast-hopping regime. We have also identified the expected temperature and magnetic-field dependences of the HFI-induced spin relaxation and diffusion, which, together with these dependence of the SOC-induced spin relaxation, can be used to uncover spin relaxation mechanisms of individual organics.

Interestingly, in the slow-hopping regime, a coherent beating of the averaged spin polarization at the frequency of the HFI field is possible. A small external magnetic field will dephase the beating and reduce the spin relaxation time.

In this paper, the HFI has been treated as a frozen magnetic field, which, as we have discussed in the paper, is not always a good approximation. It would be desirable to consider electron and nuclear spin dynamics on an equal footing, which is expected to generate interesting new physics, such as dynamical nuclear spin polarization

due to the presence of electron spins.¹¹

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