How Spin Relaxes in Bulk Halide Perovskites

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(Dated: November 1, 2022)

Spintronics in halide perovskites has drawn significant attention in recent years, due to highly tunable spin-orbit fields and intriguing interplay with lattice symmetry. Spin lifetime—a key parameter that determines the applicability of materials for spintronics and spin-based quantum information applications—has been extensively measured in halide perovskites, but not yet assessed from first-principles calculations. Here, we leverage our recently-developed ab initio density-matrix dynamics framework to compute the spin relaxation time ($T_1$) and ensemble spin dephasing time ($T_2$) in a prototype halide perovskite, namely CsPbBr$_3$, with self-consistent spin-orbit coupling and quantum descriptions of the electron scattering processes. We also implement the Landé g-factor for solids from first principles and take it into account in our dynamics, which is required to accurately capture spin dephasing under external magnetic fields. We thereby predict intrinsic spin lifetimes as an upper bound for experiments, identify the dominant spin relaxation pathways, and evaluate the dependence on temperature, external fields, carrier density, and impurities. Importantly, we find that the Fröhlich interaction that dominates carrier relaxation contributes negligibly to spin relaxation, consistent with the spin-conserving nature of this interaction. Our theoretical approach may lead to new strategies to optimize spin and carrier transport properties in spintronics and quantum information applications.

INTRODUCTION

The field of semiconductor spintronics aims to achieve the next generation of low-power electronics by making use of the spin degree of freedom. Several classes of materials for spintronic applications have been discovered, investigated and engineered in the past decade[1–5]. Efficient spin generation and manipulation require a large spin-orbit coupling (SOC), with GaAs a prototypical system, whereas long spin lifetimes ($\tau_s$), including both relaxation time ($T_1$) and dephasing time ($T_2$) (or ensemble dephasing time $T_2^*$ if inhomogeneous broadening e.g. $g$-factor inhomogeneity is present[6]), is mostly found in weak SOC materials, such as graphene and diamond. Materials with large SOC as well as long $\tau_s$ are ideal for spintronic applications but rare, presenting a unique opportunity for the discovery of new materials.

Halide perovskites, known as prominent photovoltaic[7] and light-emitting materials[8] with remarkable optoelectronic properties, have recently attracted interests also for spin-optoelectronic properties[9–14], since these materials exhibit both long lifetimes and large SOC (due to heavy elements). Compared to conventional spintronic materials, the optical accessibility for spin generation and detection of halide perovskites opens up a new avenue for spin-optoelectronics applications. Additionally, with highly tunable symmetry through the organic-inorganic framework, large Rashba splitting and high spin polarization have been realized at room temperature, critical for device applications. For example, extremely high spin polarization was produced through charge current in chiral nonmagnetic halide perovskites at room temperature in the absence of external magnetic fields[9], which is a hallmark in semiconductor spintronics. Persistent spin helix states that preserve SU(2) symmetry and that can potentially provide exceptionally long $\tau_s$ were recently discovered in two-dimensional halide perovskites[13].

Several recent experimental studies have sought to identify the dominant spin relaxation and dephasing mechanisms to further control and elongate $\tau_s$ of halide perovskites,[9–12] e.g. via time-resolved Kerr/Faraday rotations. In particular, the bulk halide perovskite such as CsPbBr$_3$, which possesses one of the simplest halide perovskite structures, is a good benchmark system to understand the fundamental physical mechanisms but already presents several outstanding questions. First, what is the intrinsic $\tau_s$ of CsPbBr$_3$? Experimentally this is not possible to isolate due to the unavoidable contributions from defects and nuclear spins. However, the intrinsic $\tau_s$ are essential as the upper limits to guide the experimental optimization of materials. Next, what scattering processes and phonon modes dominate spin relax-
ation when varying the temperature, carrier concentration, etc.? This has been extensively studied for carrier relaxation dynamics, but not yet for spin relaxation dynamics. As we show here, the role of electron-phonon (e-ph) coupling, and especially the Fröhlich interaction known to be important for carrier relaxation in halide perovskites[15], can be dramatically different in spin relaxation. Lastly, how do electron and hole $\tau_s$ respond to external magnetic fields, and what are the roles of their respective $g$-factor inhomogeneity?[10, 11]

To answer these questions, we need theoretical studies of spin relaxation and dephasing dynamics due to various scattering processes and SOC, free of experimental or empirical parameters. Previous theoretical work on spin properties of halide perovskites have largely focused on band structure and spin texture[13, 16, 17], and have not yet addressed spin relaxation and dephasing dynamics directly. Here, we apply our recently-developed first-principles real-time density-matrix dynamics (FPDM) approach[18–22] to simulate spin relaxation and dephasing times of free electrons and holes in bulk CsPbBr$_3$. We account for $ab$-initio Landé $g$-factor and magnetic momenta, self-consistent SOC, and quantum descriptions of e-ph, electron-impurity (e-i) and electron-electron (e-e) scatterings. We can therefore reliably predict $\tau_s$ with and without impurities, as a function of temperature, carrier density, and external magnetic fields. We show excellent agreement between our theoretically obtained and experimental $\tau_s$ in neat CsPbBr$_3$ crystals. We also identify important differences of the phonon contributions to carrier relaxation and spin relaxation. By answering the critical questions raised earlier, we successfully calculate the value of $\tau_s$, determine the dominant mechanism, and pave the way for optimizing and controlling spin relaxation and dephasing in halide perovskites.

RESULTS AND DISCUSSIONS

Theory

We simulate spin and carrier dynamics based on the first-principles density-matrix dynamics approach [18, 19]. We solve the quantum master equation of density matrix $\rho(t)$ as the following:[19]

$$\frac{d\rho_{12}(t)}{dt} = [H(B), \rho(t)]_{12} +$$

$$\frac{1}{2} \sum_{345} \left\{ \begin{array}{c}
[I - \rho(t)]_{13} P_{32,45} \rho_{45}(t) \\
-I - \rho(t)]_{45} P_{45,13} \rho_{32}(t)
\end{array} \right\} + H.C. \tag{1}$$

Eq. 1 is expressed in the Schrödinger picture, where the first and second terms on the right side of the equation relate to Larmor precession and scattering processes respectively. The scattering processes induce spin relaxation via the SOC. $H(B)$ is the electronic Hamiltonian at a magnetic field $B$. $[H, \rho] = H \rho - \rho H$. H.C. is Hermitian conjugate. The subindex, e.g., “1” is the combined index of k-point and band. $P$ is the generalized scattering-rate matrix considering e-ph, e-i and e-e scattering processes, computed from the corresponding scattering matrix elements and energies of electrons and phonons.

Starting from an initial density matrix $\rho(t_0)$ prepared with a net spin, we evolve $\rho(t)$ through Eq. 1 for a long enough time, typically from hundreds of ps to a few µs. We then obtain spin observable $S(t)$ from $\rho(t)$ (Eq. S1) and extract spin lifetime $\tau_s$ from $S(t)$ using Eq. S2.

Spin lifetimes at zero magnetic field

Intrinsic spin lifetimes $\tau_s$, free from crystal imperfections and nuclear spin fluctuation, is investigated first, which sets up the ideal limit for experiments. In the absence of external fields, bulk CsPbBr$_3$ possesses both time-reversal (nonmagnetic) and spatial inversion symmetries, resulting in Kramers degeneracy of a pair of bands between (pseudo-) up and down spins. Spin relaxation in such systems is conventionally characterized by Elliot-Yafet (EY) mechanism[23], where spin relaxes through spin-flip scatterings (activated by SOC). To confirm if such mechanism dominates in CsPbBr$_3$, the proportionality between $\tau_s$ and carrier lifetime ($\tau_p$, $\tau_s \propto \tau_p$) is a characteristic signature, as is discussed below. Even for intrinsic $\tau_s$, varying temperature ($T$) and carrier concentrations ($n_c$) would lead to large change, and its trend is informative for mechanism understanding.

Fig. 1 shows theoretical $\tau_s$ under zero magnetic field, including e-ph and e-e scatterings, as a function of $T$ (left) and $n_c$ (right), for free electrons and holes (SI Fig. S5). Note that although bulk CsPbBr$_3$ crystal symmetry is orthorhombic, the spin lifetime anisotropy along three principle directions is weak (see details in SI Fig. S6). Therefore only $\tau_s$ along the [001] direction is presented here. We have several major observations as summarized below.

First, a clear decay of $\tau_s$ as increasing $T$ is observed. As $\tau_s$ with and without e-e scattering (SI Fig. S5) has little difference, this indicates e-ph scattering is the dominant spin relaxation mechanism (in the absence of impurities and external magnetic fields). Note that with increasing $T$, phonon occupations increase, which enhances the e-ph scattering and thus lowers both carrier ($\tau_p$) and spin ($\tau_s$) lifetime.

Next, $\tau_s$ steeply decreases with increasing $n_c$ at low $T$ but is less sensitive to $n_c$ at high $T$ , as shown in Fig. 1b. For example, at 4K, $\tau_s$ decreases by three orders of magnitude with $n_c$ increasing from 10$^{16}$ cm$^{-3}$ to 10$^{19}$ cm$^{-3}$. Such phenomenon has been reported previously for monolayer WSe$_2$[19, 24]. The cause of such strong $n_c$-dependence at low $T$ is discussed below in more details, attributing to $n_c$ effects on (averaged) spin-flip matrix elements. As a result, at low $T$ and low $n_c$, $\tau_s$...
of CsPbBr$_3$ can be rather long, e.g., $\sim$200 ns at 10 K and $\sim$8 $\mu$s at 4 K. This is in fact comparable to the hole $\tau_s$ of transition metal dichalcogenides (TMDs) and their heterostructures[25, 26], known to be ultralong due to spin-valley locking, again suggesting the advantageous character of the halide perovskite in spintronic applications.

Importantly, good agreement between theoretical results and several independent experimental measurements is observed. Our theoretical results agree well with experimental $T_1$ of bulk CsPbBr$_3$[10] (Exp. C) assuming $n_e \approx 10^{18}$ cm$^{-3}$, and CsPbBr$_3$ nanocrystal[27] (Exp. D) assuming $n_e \approx 10^{16}$ cm$^{-3}$, respectively. We further compare theoretical results with our own measured $T_2^*$ at a weak magnetic field ($B=100$ mT; Exp. A). Excellent agreement is observed at $T \geq$20 K with $n_e$ around $10^{18}$ cm$^{-3}$ (estimated from the experimental averaged pump power). The agreement however becomes worse at $T <20$ K. As shown below in Fig. 2, the material’s imperfections could have an effect on $\tau_s$, for example e-i scattering, becoming strong below 20K and decreasing $\tau_s$ steeply. Other effect such as nuclear spin fluctuation could also be important in this experimental measurement ($T_2^*$), as discussed in the section of magnetic field effect, which may lead to additional discrepancy below 20K.

In addition, the electron and hole $\tau_s$ have the same order of magnitude (Fig. S5), consistent with experiments, but in sharp contrast to conventional semiconductors (e.g., silicon and GaAs [28]), which have longer electron $\tau_s$ than hole owing to band structure difference between valence and conduction band edges.

Fig. 2 shows the effects of impurity scattering on $\tau_s$ as a function of $T$, with four representative Pb-related defects/impurities (the results of other impurities can be found in Sec. SVI and Fig. S7). We found that even with a high impurity concentration $n_i=10^{18}$ cm$^{-3}$, which is within the experimental range of $10^{14}$-$10^{20}$ cm$^{-3}$[29–31], impurity effects are negligible at $T \geq$20 K. At lower $T$, however the presence of impurities reduces $\tau_s$, consistent with EY spin relaxation mechanism, and leads to a weaker temperature dependence of $\tau_s$ (as the e-i scattering is temperature independent). Moreover, we found that the contribution of e-i scatterings depends on the specific chemical composition of impurity, and the same defect affects differently for the electron and hole $\tau_s$. Overall, we emphasize that the quantitative description of impurity effect requires explicit atomistic simulations of impurities, given the large variation among them. They are only important under relatively low temperature $T <20$ K, with relatively high impurity density (e.g., $>10^{18}$ cm$^{-3}$).

Finally, we also predict the spin diffusion length ($l_s$) of pristine CsPbBr$_3$ in the low-density limit, which sets the upper bound of $l_s$ at different $T$. We use the relation $l_s = \sqrt{D\tau_s}$, where $D$ is diffusion coefficient obtained using the Einstein relation, with carrier mobility $\mu$ from first-principles calculations[20] (more details in Sec. SVII). Excellent agreement between theoretical and experimental carrier mobility is found for CsPbBr$_3$ (SI Fig.S8a). We find $l_s$ is longer than 10 nm at 300 K, and possibly reach tens of $\mu$m at $T \leq 10$ K (see details in Sec. SVII and Fig. S8 in SI).

Analysis of spin-phonon relaxation

To gain deep mechanistic insights, we next analyze different phonon modes and carrier concentration effects on spin relaxation through examining spin-resolved e-ph matrix elements.

In Fig. 3, we compare the contribution of different phonon modes to $\tau_s$ and $\tau_p$. First, we find that at a very low $T \sim 4$ K, only acoustic modes (A1-A3) contribute to spin and carrier relaxation. This is simply because the optical phonons are not excited at such low $T$ (corresponding $k_BT \sim$0.34 meV much lower than optical energy $\gtrsim 2$ meV). At $T \geq$10 K, optical modes are more important for both spin and carrier relaxation (green and blue dashed lines closer to black line (all phonons) in Fig. 3).

In particular, from Fig. 3b, we find that two special optical modes - 57th and 58th modes (O57-O58, modes ordered by phonon energy with their phonon vector plots in SI Fig. S3) dominate carrier relaxation at $T \geq$50 K, because carrier lifetime $\tau_p$ due to O57-O58 (blue dashed line) nearly overlaps with $\tau_p$ due to all phonon modes (black line). These two optical phonon modes are mixture of longitudinal and transverse vibration as shown in SI Fig. S3. In contrast, for spin relaxation in Fig. 3a, at $T \geq$10 K O57-O58 are less important than other optical modes (green dashed line). More specifically, in this temperature range, there are tens of phonon modes (with energies ranging from 2 meV to 18 meV), contributing similarly to spin relaxation. This is contradictory to the simple assumption frequently employed in previous experimental studies[10, 32, 33] that a single longitudinal optical (LO) phonon with a relatively high energy (e.g. $\sim$18 meV for CsPbBr$_3$ in Ref.10) dominates spin relaxation over a wide $T$ range, e.g., from 50 K to 300 K, through a Fröhlich type e-ph interaction.

In the simplified picture of Fermi’s golden rule (FGR), $\tau_s^{-1}$ and $\tau_p^{-1}$ (due to e-ph scattering) are proportional to the modulus square of spin-flip ($|g\tilde{\tau}_{\uparrow\downarrow}|^2$) and spin-conserving ($|g\tilde{\tau}_{\uparrow\uparrow}|^2$) matrix elements (ME), respectively. From Fig. 4a, we find that spin-flip ME is dominated by “other optical modes” (blue line), opposite to the spin-conserving ME in Fig. 4b (i.e. instead, dominated by special optical phonon modes O57 and O58 (red line)). This well explains the different roles of optical O57-O58 modes in carrier and spin relaxation. Moreover, spin-conserving ME for O57-O58 in Fig. 4b diverges at $q \rightarrow 0$, which indicates its dominant long-range nature, consistent with the common long-range Fröhlich interaction picture[34], mostly driving carrier relaxation in polar materials at high $T$ (e.g., 300 K). On the contrary, the small magni-
FIG. 1. Spin lifetimes $\tau_s$ due to both the electron-phonon (e-ph) and electron-electron (e-e) scatterings of electrons of pristine CsPbBr$_3$ (a) calculated as a function of $T$ at different electron densities $n_e$ compared with experimental data and (b) calculated as a function of $n_e$ at different $T$. We compare electron and hole $\tau_s$ in Supplementary information (SI) Fig. S5 and they have the same order of magnitude at all conditions we investigated. Exp. A are our experimental data of spin lifetimes of bulk CsPbBr$_3$ under a small external transverse magnetic field. For Exp. A, the density of photo-excited carriers is estimated to be about $10^{18}$ cm$^{-3}$. Exp. B are experimental data of exciton $\tau_s$ of CsPbBr$_3$ films from Ref. 12. Exp. C and Exp. D are experimental data of spin relaxation time $T_1$ of bulk CsPbBr$_3$ and CsPbBr$_3$ nanocrystals measured by the spin inertia method from Ref. 10 and 27 respectively. For Exp. C and D, the measured lifetimes cannot be unambiguously ascribed to electrons or holes and can be considered as values between electron and hole $T_1$. The carrier densities are not reported for Exp. C and D. The vertical dashed line in panel (b) corresponding to $n_e$ with chemical potential $\mu_{F,c}$ at the conduction band minimum (CBM).

tude of spin-flip ME for O57-O58 modes indicates that Fröhlich interaction is unimportant for spin relaxation. This important conclusion again emphasizes the sharp difference between spin and carrier relaxations in polar materials.

To explain the strong $n_e$ dependence of $\tau_s$ at low $T$, we further analyze the $T$ and chemical potential ($\mu_{F,c}$) dependent effective spin-flip ME $|\tilde{g}^{\uparrow \downarrow}|^2$ (averaged around $\mu_{F,c}$, see Eq. 12) and scattering density of states $D_S$ (Eq. 15). In FGR, we have the approximate relation in Eq. 16, i.e. $\tau_s^{-1} \propto |\tilde{g}^{\uparrow \downarrow}|^2 D_S$.

In Fig. 4c, we show the $n_e$ dependence of $\tau_s^{-1}$, compared with $|\tilde{g}^{\uparrow \downarrow}|^2$ and $|\tilde{g}^{\uparrow \downarrow}|^2 D_S$. Indeed we can see $\tau_s^{-1}$ and $|\tilde{g}^{\uparrow \downarrow}|^2 D_S$ nearly overlapped, as the result of Eq. 16. The strong increase of $\tau_s^{-1}$ at $n_e > 10^{16}$ cm$^{-3}$ can be attributed to the fact that both spin-flip ME $|\tilde{g}^{\uparrow \downarrow}|^2$ and scattering density of states $D_S$ increase with $n_e$. Interestingly, the effective spin-conserving ME $|\tilde{g}^{\uparrow \downarrow}|^2$, most important in carrier relaxation, decreases with $n_e$, opposite to spin-flip $|\tilde{g}^{\uparrow \downarrow}|^2$. This again emphasizes the e-ph scattering affects carrier and spin relaxation differently, given the opposite trends of spin-conserving and spin-flip scattering as a function of $n_e$. When $n_e < 10^{16}$ cm$^{-3}$, $\tau_s^{-1}$ is insensitive to $n_e$, which is because both $|\tilde{g}^{\uparrow \downarrow}|^2$ and $D_S$ are determined by e-ph transitions around the band edge. In “Methods” section, we have proven that at the low density limit, since carrier occupation satisfies Boltzmann distribution, both $|\tilde{g}^{\uparrow \downarrow}|^2$ and $D_S$ are $\mu_{F,c}$ and $n_e$ independent.

Landé $g$-factor and magnetic field effects

Under a magnetic field $\mathbf{B}$, the electronic Hamiltonian reads

$$H_k(\mathbf{B}) = H_{0,k} + \mu_B \mathbf{B} \cdot (\mathbf{L}_k + g_0 \mathbf{S}_k),$$

where $\mu_B$ is Bohr magneton; $g_0$ is the free-electron $g$-factor; $\mathbf{S}$ and $\mathbf{L}$ are the spin and orbital angular momentum respectively. The simulation of $\mathbf{L}$ is nontrivial for periodic systems and the details are given in Method section and Ref. [35]. Having $H (\mathbf{B})$ at a transverse $\mathbf{B}$ perpendicular to spin direction, $T_2^*$ is obtained by solving the density-matrix master equation in Eq. 1. Here we consider only transverse $\mathbf{B}$, since longitudinal $\mathbf{B}$ has negligible effects on spin dynamics without considering nuclear spins, magnetic impurities, or quantum interference effects[36].

The key parameters for the description of the magnetic-field effects are the Landé $g$-factors. Their values relate to $\mathbf{B}$-induced energy splitting (Zeeman effect) $\Delta E_k (\mathbf{B})$ and Larmor precession frequency $\Omega_k$, satisfying
FIG. 2. Spin lifetime $\tau_s$ of (a) electrons and (b) holes in CsPbBr$_3$ calculated with and without neutral impurities at concentration of $10^{18}$ cm$^{-3}$. Here carrier density $n_c$ is at $10^{18}$ cm$^{-3}$. V$_{\text{Pb}}$ denotes Pb vacancy; Pb$_{\text{Br}}$ and Pb$_{\text{Cs}}$ denote Pb substitution of Br or Cs atoms; Pb$_i$ denotes an extra Pb atom at an interstitial site. The effects of other defects or impurities are given in Supplementary information (SI).

$\Omega_k \approx \Delta E_k = \mu_B B \tilde{g}_k$ with $\tilde{g}_k$ the $k$-resolved Landé g-factor. More importantly, the g-factor fluctuation (near Fermi surface or $\mu_{F,c}$) leads to spin dephasing under $\mathbf{B}$, corresponding to $T_2^s$.

Fig. 5a shows $\tilde{g}_k$ of electrons and holes at $k$-points around the band edges. $\tilde{g}_k$ are computed using $\Delta E_k(\mathbf{B})$ (Eq. 8 and 9) obtained from $H_k(\mathbf{B})$. Our calculated electron $\tilde{g}_k$ are larger than hole $\tilde{g}_k$, and the sum of electron and hole $\tilde{g}_k$ range from 1.85 to 2.4, in agreement with experiments[10, 28]. Furthermore, $\tilde{g}_k$ are found sensitive to state energies and wavevectors $\mathbf{k}$, and the fluctuation of $\tilde{g}_k$ is enhanced with increasing the state energy. In Figs. 5b and 5c, we show the global g-factor $[g_{3\Omega}]$ and the amplitude of the g-factor fluctuation (near the Fermi surface) $\Delta \tilde{g}$ (Eq. 11) as a function of $n_c$. Both $[g_{3\Omega}]$ and $\Delta \tilde{g}$ are insensitive to $n_c$ at $n_c < 10^{16}$ cm$^{-3}$, but sensitive to $n_c$ at $n_c \geq 10^{16}$ cm$^{-3}$.

In Fig. 5, we show ab-initio g-factors computed with the PBE functional[37]. We further compare g-factors computed using different exchange-correlation functionals ($V_{xc}$) in SI Sec.SV where we find strong $V_{xc}$ dependence. For example, the sign of hole g-factor changes from negative at PBE to positive at EV93PW91. The latter functional gives improved band gaps. Similar $V_{xc}$ dependence also appears in g-factor anisotropy along three principle directions as discussed in SI Sec.SV. Our results indicate that accurate electronic structure is important for quantitative evaluation of g-factors. On the other hand, $T_2^s$ only depends on g-factor fluctuation $\Delta \tilde{g}$, which is much less sensitive to $V_{xc}$.

Next, we discuss magnetic-field effects on $\tau_s$ in Fig. 6, calculated from our FPDM approach, and analyze them with phenomenological models. Under $\mathbf{B} = BB$ ($\mathbf{B}$ is a unit vector), the total spin decay rate is approximately expressed by

$$\tau_s^{-1}(\mathbf{B}) \approx \left(\tau_s^0\right)^{-1} + \left(\tau_s^{\Delta \Omega}\right)^{-1}(\mathbf{B}),$$

where $\left(\tau_s^0\right)^{-1}$ is the zero-field spin relaxation rate due to EY mechanism; $\left(\tau_s^{\Delta \Omega}\right)^{-1}$ is induced by the Larmor-precession-frequency fluctuation $\Delta \tilde{g}$, and can be described by different mechanisms depending on the magnitude of $\tau_p \Delta \Omega$[6, 23]:

(i) Free induction decay (FID) mechanism if $\tau_p \Delta \Omega \gtrsim 1$ (weak scattering limit).
We have

$$\left(\tau_s^{\Delta \Omega}\right)^{-1} \sim \left(\tau_s^{\text{FID}}\right)^{-1} \sim C^{\Delta \tilde{g}} \Delta \Omega = C^{\Delta \tilde{g}} \mu_B B \Delta \tilde{g},$$

where $C^{\Delta \tilde{g}}$ is a constant and often taken as 1 or $1/\sqrt{2} \approx 0.71[6, 10, 32, 38–41]$. The latter assumes a
FIG. 5. The Landé 𝑔-factor of electron and holes for magnetic fields along [110] direction calculated at the PBE functional. (a) The 𝑘-dependent 𝑔-factor 𝑔̃(Eq. 8 and 9) at 𝑘 points around the band edges. Each data-point corresponds to a 𝑘 point. (b) The absolute value of the global 𝑔-factor defined as |𝑔| = 𝑄/μ𝐵𝐵 as a function of 𝑛𝑒, where 𝑄 is Larmor precession frequency extracted from spin dynamics under the magnetic field. g| is very similar to the absolute value of the averaged 𝑔-factor |g| defined in Eq. 10. (c) The effective amplitude of the fluctuation of 𝑔 factors - ∆g defined in Eq. 11 as a function of carrier density at 10 K.

As a result, we only discuss 𝑡𝑠 under magnetic field below 20 K, specifically at 4K afterwards. From Fig. 6b, we can see that magnetic-field effects on electron and hole 𝑡𝑠 are quite similar, which is a result of their similar band curvatures, e-ph scattering, and ∆g (Fig. 5c), although their absolute 𝑔-factors are quite different, as shown in Fig. 5a and 5b.

We further examine magnetic-field effects on 𝑡𝑠 at 4 K without (and with) the e-i scattering in Fig. 6c (and 6d). As discussed above, 𝑡𝑠−1(𝐵) increases with 𝐵. More specifically, we find that the calculated 𝑡𝑠−1(𝐵) is proportional to 𝐵2 under low 𝐵 (details in SI Fig. S9) following the DP mechanism (Eq. 5), but linear to 𝐵 under higher 𝐵 following the free induction decay mechanism (Eq. 4).

The comparison of calculated 𝑡𝑠−1(𝐵) with experimental data (orange diamond in Fig. 6b) is reasonable with 𝑛𝑒 around 1018 cm−3 (the experimental estimated average carrier concentration). However, their 𝐵-dependence is not the same in the small 𝐵 field range, e.g. under 𝐵 < 0.4 Tesla, the calculated 𝑡𝑠−1(𝐵) is proportional to 𝐵2 (as shown in SI Fig. S9), whereas the experimental 𝑡𝑠−1(𝐵) is more likely linear to 𝐵. In principles, extremely small 𝐵 field will lead to ∆Ω small enough falling in the DP regime ((𝑡𝑠−1(𝐵)) proportional to 𝐵2). The fact that experimental results still keep in the FID regime ((𝑡𝑠−1(𝐵)) linear dependent on 𝐵) under small 𝐵 field implies additional internal 𝐵 field fluctuation contributes to ∆Ω when external 𝐵 is small. It may originate from nuclear spin fluctuation, magnetic impurities, carrier localization, chemical potential fluctuation, etc.[10, 28] in samples, which are however beyond the scope of this work.

Moreover, in Fig. 6c (and d), we find that under finite 𝐵, 𝑡𝑠 decreases with 𝑛𝑒, similar to the case under the zero-field. But the origin of the strong 𝑛𝑒 dependence

Gaussian distribution of 𝑔-factors and the scattering being completely absent[6, 39, 41].

(ii) Dyakonov Perel (DP) mechanism if 𝑡𝑠∆Ω ≪ 1 (strong scattering limit). We have

\[ (\tau_s^{\Delta \Omega})^{-1} \sim (\tau_s^{DP})^{-1} \sim \tau_p \langle \Delta \Omega \rangle^2 = \tau_p (\mu_B B \Delta \tilde{g})^2. \]  

(iii) Between (i) and (ii) regimes, there isn’t a good approximate relation for \((\tau_s^{\Delta \Omega})^{-1}\), but we may expect that[6]

\[ (\tau_s^{DP})^{-1} \lesssim (\tau_s^{\Delta \Omega})^{-1} \lesssim (\tau_s^{FID})^{-1}. \]

From Fig. 6a, we find that magnetic-field effects are weak (\(\tau_s(\mathbf{B})/\tau_s(0) \approx 1\)) at 𝑇 ≥ 20 K. This is because at high 𝑇, e-ph scattering is weak which leads to short 𝑡𝑝 and short spin lifetime at zero field \(\tau_s^0\) (large \(\tau_s^{\Delta \Omega} (\tau_s^{DP})\)). Then the spin relaxation falls into strong or intermediate scattering regimes ((ii) or (iii)), which give small \((\tau_s^{\Delta \Omega})^{-1}\). Finally, following \((\tau_s^{\Delta \Omega})^{-1} \ll (\tau_s^0)^{-1}\) obtained above, we reach \(\tau_s(\mathbf{B})/\tau_s(0) \approx 1\) from Eq. 3.

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FIG. 6. The effects of transverse magnetic fields (perpendicular to spin direction) on calculated $\tau_s$ of free carriers of CsPbBr$_3$.

(a) The ratio of $\tau_s$ under $B=1$ T and $\tau_s$ under $B=0$ as a function of $T$. Here electron carrier concentration $n_e=10^{18}$ cm$^{-3}$.

(b) Spin decay rates ($\tau_s^{-1}$) of electrons and holes as a function of $B$ at 4 K with $n_c=10^{18}$ cm$^{-3}$. (c) and (d) are $\tau_s^{-1}$ as a function of $B$ at 4 K at different $n_e$ (c) without and (d) with $10^{17}$ cm$^{-3}$ Pb neutral impurities. “Exp.” (orange open diamond) represent our experimental data (with the B field along [010] direction), where the density of photo-excited carriers is estimated about $10^{18}$ cm$^{-3}$. The orange dashed line is the linear fit of experimental data. The linear relation between ensemble spin dephasing rate and $B$ was frequently found and used in previous experimental measurements[10, 32, 38, 39].

CONCLUSIONS

Through a combined ab-initio theory and experimental study, we reveal the spin relaxation and dephasing mechanism of carriers in halide perovskite. Using our FPDM approach and implementing ab-initio magnetic moments and $g$-factor, we simulate free-carrier $\tau_s$ as a function of temperature and magnetic fields, in excellent agreement with experiments. We predict $\tau_s$ of pristine CsPbBr$_3$ at different $T$ and $n_c$, which approximately set the upper time scale (and further determine the upper length scale) on which CsPbBr$_3$-based spintronic devices can operate. Ultraslow spin relaxation in pristine CsPbBr$_3$ is predicted at low $T$, e.g., $\sim200$ ns at 10 K and $\sim8$ $\mu$s at 4 K. We find $\tau_s$ is strongly $n_c$ dependent especially at low $T$, e.g. $\tau_s$ can be tuned by three order of magnitude with $n_c$ from the low density limit to $10^{19}$ cm$^{-3}$. Under high $B$ is very different from $\tau_s$ under zero-field. When $B \geq 0.4$ Tesla, $\tau_s$ is dominated by the FID mechanism (Eq. 4), thus its $n_c$ dependence is mostly from $\Delta g$'s strong $n_c$ dependence shown in Fig. 5c.

Finally, by comparing Fig. 6c and 6d, we conclude that introducing more scattering such as adding impurities, weakens the $B$-dependence ($\tau_s^{-1}$ increases slower with increasing $B$). The explanation is as follows. More scatterings lead to smaller $\tau_p$ (thus smaller $\tau_p \Delta \Omega$, $(\tau_s^{\Delta \Omega})^{-1}$ closer to strong scattering limit in regime (ii), dominated by DP mechanism $(\tau_s^{DP})^{-1}$). The latter is often much smaller than FID rate $(\tau_s^{FID})^{-1}$ in regime (i) (the weak scattering limit). Meanwhile, more impurity scatterings give large zero-$B$ field spin relaxation rate $(\tau_s^0)^{-1}$. Together, increasing external scatterings, leading to an increase of $(\tau_s^0)^{-1}$ and a decrease of $(\tau_s^{\Delta \Omega})^{-1}$, finally weakens the $B$-dependence of $\tau_s^{-1}$ ($B$).
Understanding the dependence of $\tau_s$ on $T$ and $n_c$ is critical for determining the optimal conditions for spintronic applications.

From our detailed e-ph matrix element analysis, we find that contrary to common belief, Fröhlich interaction is unimportant to spin relaxation, although critical for carrier relaxation. Finally, we find that magnetic-field effects are only significant under $T<20$ K. The strong $n_c$ dependence of $\tau_s$ under finite $B$ is originated from large change of $\Delta g$, fundamentally different from the case under zero magnetic field. Our work provides fundamental insights on how to control and manipulate spin relaxation in halide perovskites, which are vital for their spintronics and quantum information applications.

**METHODS**

**Spin dynamics and transport.** Spin dynamics and spin lifetime $\tau_s$ are simulated by our recently developed first-principles density-matrix dynamics (FPDM) method\[18–22\]. Starting from an initial state with a spin imbalance, we evolve the time-dependent density matrix $\rho(t)$ through the quantum master equation with Lindblad dynamics for a long enough simulation time, typically from us to $\mu$, varying with systems. After obtaining spin observable $S(t)$ from $\rho(t)$ and fitting $S(t)$ to an exponentially oscillating decay curve, the decay constant $\tau_s$ and the precession frequency $\Omega$ are then obtained (Eq. S2 and Fig. S1 in SI). All required quantities of FPDM simulations, including electron energies, phonon eigensystems, e-ph and e-i scattering matrix elements, are calculated on coarse $k$ and $q$ meshes using the DFT open source software JDFTX\[42\], and then interpolated to fine meshes in the basis of maximally localized Wannier functions\[43–45\]. The e-e scattering matrix is computed using the same method given in Ref. 19. More theoretical background and technical details are given in Ref. 20 and 19, as well as the Supporting Information.

Using the same first-principles electron and phonon energies and matrix elements on fine meshes, we calculate the carrier mobility by solving the linearized Boltzmann equation using a full-band relaxation-time approximation\[46\] and further estimate spin diffusion length based on the drift-diffusion model (SI Sec. SVII).

**Orbital angular momentum.** With the Bloch basis, the orbital angular momentum reads

$$L_{k,mn} = i \left( \frac{\partial \varphi_{km}}{\partial k} \right)^* \left( \hat{H}_0 - \frac{\epsilon_{km} + \epsilon_{kn}}{2} \right) \left( \frac{\partial \varphi_{kn}}{\partial k} \right),$$

where $m$ and $n$ are band indices; $\epsilon$ and $u$ are electronic energy and the periodic part of the wavefunction, respectively; $\hat{H}_0$ is the zero-field Hamiltonian operator. Eq. 7 can be proven equivalent to $L = 0.5 \ast (r \times p - p \times r)$ with $r$ and $p$ the position and momentum operator respectively. The detailed implementation of Eq. 7 is described in Ref. 35. Our implementation of $L$ has been benchmarked against previous theoretical and experimental data for monolayer MoS$_2$ (Table S1).

**g-factor of free carriers.** In experimental and model Hamiltonian theory studies\[10, 28\], g-factor is defined from the ratio between either $B$-induced energy splitting $\Delta E(B)$ or Larmor precession frequency $\Omega(B)$ to $\mu B$. Therefore, we define $g$-factor of an electron or a hole at state $k$,

$$g^S_k = \theta^S_k (\hat{B}) \frac{\Delta E_k(B)}{\mu B},$$

where $g^S_k$ is $g$-factor defined based on spin expectation values. $\Delta E_k(B)$ is the energy splitting due to finite $B$. $\theta^S_k (\hat{B})$ is the sign of $S^\text{exp}_{k,h} (\hat{B}) - S^\text{exp}_{k,l} (\hat{B})$, where $S^\text{exp}_{k,h} (\hat{B})$ and $S^\text{exp}_{k,l} (\hat{B})$ are the spin expectation value (exp) of the higher (h) and lower (l) energy band at $k$ projected to the direction of $\hat{B}$ respectively.

However, in previous theoretical studies of perovskites\[28, 47\], g-factors were defined based on pseudo-spins related to the total magnetic momenta $J^\text{tot}$, which are determined from the atomic-orbital models. The pseudo-spins can have opposite directions to the actual spins. Most previous experimental studies adopted the same convention for the signs of carrier g-factors. Therefore, to compare with $g$-factors obtained in previous theoretical and experimental studies, we introduce a correction factor $C^{S \rightarrow J}$ and define a new $g$-factor:

$$\bar{g}_k (\hat{B}) = C^{S \rightarrow J} g^S_k.$$  

$C^{S \rightarrow J} = m^S_{k,h}/m^S_{k,l}$ with $m^S_{k,h}$ and $m^S_{k,l}$ the total and spin magnetic moments respectively, obtained from the atomic-orbital model\[28\]. $C^{S \rightarrow J}$ is independent from $k$-point, and is $\mp 1$ for electrons and holes respectively for CsPbBr$_3$.

$\bar{g}_k$ is different at different $k$; therefore we define its statistically averaged value (depending on temperature $T$ and chemical potential $\mu_{e,c}$) as

$$\bar{g} = \frac{\sum_k (\mp f^J_k \bar{g}_k)}{\sum_k (\mp f^J_k)},$$

and its fluctuation amplitude as

$$\Delta \bar{g} = \sqrt{\frac{\sum_k (\mp f^J_k) (\bar{g}_k - \bar{g})^2}{\sum_k (\mp f^J_k)}},$$

where $f^J_k$ is the derivative of the Fermi-Dirac distribution function. Here for simplicity the band index of $f^J_k$ is dropped considering both valence and conduction bands are two-fold degenerate.

We have further defined a more general $g$-factor as a tensor and its fluctuation amplitude in SI Sec. SV. For CsPbBr$_3$, we find different definitions predict quite similar values (differences are not greater than 10%).
Analysis of e-ph matrix elements. For EY spin relaxation, in the simplified picture of Fermi’s golden rule (FGR), $\tau_{s}^{-1}$ is proportional to the modulus square of the spin-flip scattering matrix element. As the e-ph scattering plays a crucial role in spin relaxation in CsPbBr$_3$, it is helpful to analyze the spin-flip e-ph matrix elements.

Note that most matrix elements are irrelevant to spin relaxation and we need to pick the “more relevant” ones, by defining a weight function related to occupation and energy conservation. Therefore we propose a $T$ and $\mu_{F,c}$ dependent effective modulus square of the spin-flip e-ph matrix element $\langle g^\dagger g \rangle^2$ as

$$\langle g^\dagger g \rangle^2 = \sum_{kq} w_{k,k-q} \sum_{\lambda} |g_{k,k,q}^{\lambda}|^2 n_{q\lambda}, \quad (12)$$

$$w_{k,k-q} = f_{k-q} (1 - f_k) \delta (\epsilon_k - \epsilon_{k-q} - \omega_c), \quad (13)$$

where $g_{k,k-q}^{\lambda}$ is e-ph matrix element, related to a scattering event between two electronic states of opposite spins at $k$ and $k - q$ through phonon mode $\lambda$ at wavevector $q$; $n_{q\lambda}$ is phonon occupation; $f_k$ is Fermi-Dirac function; $\omega_c$ is the characteristic phonon energy specified below, and $w_{k,k-q}$ is the weight function. Here we drop band indices for simplicity, as CsPbBr$_3$ bands are twofold Kramers degenerate and only two bands are relevant to electron and hole spin/carrier dynamics.

The matrix element modulus square is weighted by $n_{q\lambda}$ since $\tau_{s}^{-1}$ is approximately proportional to $n_{q\lambda}$ according to Eq. 5 of Ref. 18. This rules out high-frequency phonons at low $T$ which are not excited. $\omega_c$ is chosen as 4 meV at 10 K based on our analysis of phonon-mode-resolved contribution to spin relaxation. The trends of $\langle g^\dagger g \rangle^2$ are found not sensitive to $\omega_c$ as checked. $w_{k,k-q}$ selects transitions between states separated by $\omega_c$ and around the band edge or $\mu_{F,c}$, which are “more relevant” transitions to spin relaxation.

We also define a $q$-resolved modulus square of the spin-flip e-ph matrix element $\langle g^\dagger g \rangle^2 (q)$ as

$$\langle g^\dagger g \rangle^2 (q) = N_k^{-1} \sum_{k,\lambda} |g_{k,k,q}^{\lambda}|^2 n_{q\lambda}. \quad (14)$$

Note that for spin relaxation, only states around the band edges are relevant. Thus we restrict $|\epsilon_k - \epsilon_{\text{edge}}| < 180$ meV for the calculation of Eq. 14, which is about 7 $k_B T$ at 300 K relative to the band edge energy ($\epsilon_{\text{edge}}$).

Analysis of the EY spin relaxation rate. According to FGR, the EY spin relaxation rate of an electronic state should be also proportional to the density of pair states allowing spin-flip scattering between them. Therefore, we propose a scattering density of states $D^S$ (which is $T$ and $\mu_{F,c}$ dependent),

$$D^S(T, \mu_{F,c}) = \frac{2N_k^{-2} \sum_{kq} w_{k,k-q}}{N_k^{-1} \sum_k f_k (1 - f_k)}. \quad (15)$$

$D^S$ can be regarded as an effective density of spin-flip or spin-conserving e-ph transitions satisfying energy conservation between one state and its pairs (considering that the number of spin-flip and spin-conserving transitions are the same for Kramers degenerate bands).

When $\omega_c = 0$ (i.e. elastic scattering), we have $D^S = \int d\epsilon \left( -\frac{df}{d\epsilon} \right) D^2 (\epsilon)$ for density of electronic states (DOS). So $D^S$ can be roughly regarded as an weighted averaged DOS with weight $\left( -\frac{df}{d\epsilon} \right) D (\epsilon)$.

With $\langle g^\dagger g \rangle^2$ and $D^S$, we have the approximate relation for spin relaxation rate,

$$\tau_{s}^{-1} \propto \langle g^\dagger g \rangle^2 D^S. \quad (16)$$

We then discuss $\mu_{F,c}$ dependence of $\tau_{s}^{-1}$ at low $n_c$ limit. For simplicity, we only consider conduction electrons. At low $n_c$ limit, we have $\exp (\mu| - \mu_{F,c} |/ (k_BT)) \gg 1$, thus

$$f_{k-q} (1 - f_k) \approx \exp (\frac{\mu_{F,c}}{k_BT}) \exp \left( \frac{-\epsilon_{k-q}}{k_BT} \right). \quad (17)$$

Therefore, according to Eq. 12, 13 and 15, both $\langle g^\dagger g \rangle^2$ and $D^S$ are independent from $\mu_{F,c}$ (as $\exp \left( \frac{\mu_{F,c}}{k_BT} \right)$ is cancelled out), so $\tau_{s}^{-1}$ is independent from $\mu_{F,c}$ and $n_c$ at low $n_c$ region, e.g. much lower than $10^{10}$ cm$^{-3}$ for CsPbBr$_3$. We can similarly define spin conserving matrix elements $\langle g^\dagger g \rangle^2 (q)$ by replacing $g_{k,k-q}^{\lambda}$ to $g_{k,k-q}^{\lambda}$ in Eq. 12 and 14. Then we have the approximate relation for carrier relaxation rate due to e-ph scattering, $\tau_{\rho}^{-1} \propto \langle g^\dagger g \rangle^2 D^S$.

Experimental synthesis. Growth of CsPbBr$_3$ single crystal: Small CsPbBr$_3$ seeds were first prepared with fresh supersaturated precursor solution at 85 °C. Small and transparent seeds were then picked and put on the bottom of the vials for large crystal growth. The temperature of the vials was set at 80 °C initially with an increasing rate of 1 °C/h, and was eventually maintained at 85 °C. Vials were covered with glass slides to avoid fast evaporation of the DMSO solvent. After 120-170 hours, a centimeter-sized single crystal was picked from the solution, followed by wiping the residue solution on the surface.

Experimental Spin Lifetime Measurement. For measuring the spin lifetime in CsPbBr$_3$ single crystals, we have used the ultrafast circularly-polarized photoinduced reflectivity (PPR) method at liquid He temperature under the influence of a magnetic field. The experimental setup was described elsewhere[48, 49]. It is a derivative of the well-known ‘pump-probe’ technique, where the polarization of the pump beam is modulated by a photoelastic modulator between left ($\delta^+$) and right ($\delta^-$) circular polarizations, namely LCP and RCP, respectively. Whereas the probe beam is circularly polarized (either LCP or RCP) by a quarter-wave plate. The transient change in the probe reflection, namely c-PPR(t), was recorded.
The 405 nm pump beam, having 150 femtoseconds pulse duration at 80 MHz repetition rate, was generated by frequency doubling the fundamental at 810 nm from the Ti:Sapphire laser (Spectra Physics) using a SHG BBO crystal. The 533 nm probe beam was generated by combining the 810 nm fundamental beam with the 1560 nm infrared beam from an OPA (optical parametric amplifier) onto a BBO type 2 SFG (Sum Frequency Generation) crystal. The pump/probe beams having average intensity of $12 \text{Wcm}^{-2}$ and $3 \text{Wcm}^{-2}$, respectively were aligned onto the CsPbBr$_3$ crystal that was placed inside a cryostat with a built-in electro-magnet that delivered a field strength, $B$ up to 700 mT at temperatures down to 4 K. Using this technique we measured both t-PPR responses at both zero and finite $B$ to extract the $B$-dependent electron and hole spin lifetimes. From the c-PPR($B,t$) dynamics measured on (001) facet with B directed along [010][49] (see example c-PPR($B,t$) dynamics in SI Fig. S10), we could obtain the electron and hole $T^*_2$ by fitting the transient quantum beating response with two damped oscillation functions:

$$A_1 e^{-\frac{t}{T^*_2,e}} \cos(2\pi f_1 t + \phi_1) + A_2 e^{-\frac{t}{T^*_2,h}} \cos(2\pi f_2 t + \phi_2),$$

where $T^*_2,e$ and $T^*_2,h$ are the spin dephasing times of the electrons and holes; $f_1$ and $f_2$ are the two QB frequencies that can be obtained directly from the fast Fourier transform of the c-PPR dynamics.

**DATA AVAILABILITY**

All relevant data are available from the authors upon request.

**CODE AVAILABILITY**

The codes are available through open-source software, JDFTx[42] and QUANTUM ESPRESSO[50], or from authors upon request.

**ACKNOWLEDGEMENTS**

Ping and Sundararaman acknowledge the support from National Science Foundation under grant No. DMR-1956015. Ping also acknowledge the support from the Air Force Office of Scientific Research under AFOSR Award No. FA9550-21-1-0087. The spectroscopic measurements and the single-crystal growth were supported by the Center for Hybrid Organic-Inorganic Semiconductors for Energy (CHOISE), an Energy Frontier Research Center funded by the Office of Basic Energy Sciences, Office of Science within the US Department of Energy through contract number DE-AC36-08GO28308. This research used resources of the Center for Functional Nanomaterials, which is a US DOE Office of Science Facility, and the Scientific Data and Computing center, a component of the Computational Science Initiative, at Brookhaven National Laboratory under Contract No. DE-SC0012704, the lux supercomputer at UC Santa Cruz, funded by NSF MRI grant AST 1828315, the National Energy Research Scientific Computing Center (NERSC) a U.S. Department of Energy Office of Science User Facility operated under Contract No. DE-AC02-05CH11231, and the Extreme Science and Engineering Discovery Environment (XSEDE) which is supported by National Science Foundation Grant No. ACI-1548562 [51].

**AUTHOR CONTRIBUTIONS**

J.X. and K.L. performed the ab-initio calculations; J.X., K.L., R.S. and Y.P. analyzed the theoretical results. J.X. and R.S. implemented the computational codes. U.N.H., J.H. and V.V. did the experimental measurements. Y.P. designed and supervised all aspects of the study. J.X and Y.P. wrote the first draft of the manuscript. All authors contributed to the writing of the manuscript.

**COMPETING INTERESTS**

The authors declare no competing interests.

**ADDITIONAL INFORMATION**

Supplementary information is available for this paper at [url]. Correspondence and requests for materials should be addressed to J.X., R.S. or Y.P.

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Supplementary information for: How Spin Relaxes in Bulk Halide Perovskites

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\textbf{SI. THE SIMULATION OF SPIN LIFETIME} \\

Spin lifetime is calculated based on the method developed in Ref. ? \textsuperscript{17}. To define spin lifetime, we follow the time evolution of the observable

\[ S_i(t) = \text{Tr} (s_i (t) \rho(t)) \tag{S1} \]

where \( \rho(t) \) is the density matrix; \( s_i \) is spin Pauli matrix in Blöch basis along direction \( i \). This time evolution must start at an initial state (at \( t = t_0 \)) with a net spin i.e. \( \delta \rho(t_0) = \rho(t_0) - \rho_{\text{eq}} \neq 0 \) such that \( \delta S_i(t_0) = S_i(t_0) - S_{i,eq} \neq 0 \), where “eq” corresponds to the final equilibrium state. We evolve the density matrix through the quantum master equation given in Ref. \textsuperscript{21} (Eq. 5 therein) for a long enough simulation time, typically from \( \text{ns} \) to \( \mu \text{s} \), until the evolution of \( S_i(t) \) can be reliably fitted by

\[ S_i(t) - S_{i,eq} = [S_i(t_0) - S_{i,eq}] \exp \left[ -\frac{t - t_0}{\tau_{s,i}} \right] \times \cos [\Omega (t - t_0) + \phi] \tag{S2} \]

to extract the spin lifetime, \( \tau_{s,i} \). Above, \( \Omega \) is oscillation frequency due to energy splitting in general, which under an applied magnetic field \( B \) would have a magnitude of about \( \mu_B \vec{B} \vec{g} \), where \( \vec{g} \) is the weighted averaged \( g \)-factor defined in Eq. 9 in the main text.

In Ref. \textsuperscript{22}, we have shown that it is suitable to generate the initial spin imbalance by applying a test magnetic field at \( t = -\infty \), allowing the system to equilibrate with a net spin and then turning it off suddenly at \( t_0 \).
FIG. S1. Time evolution of $S_z$ of pristine CsPbBr$_3$ at 4 K under a transverse magnetic field of 0.5 Tesla $n_c = 10^{18}$ cm$^{-3}$, after the initial spin imbalance generated by a test magnetic field. “Calc.” denotes calculated $S_z$. “Fit” denotes fitted $S_z$ using Eq. S2.

In Fig. S1, we compare calculated $S_z$ and fitted ones using Eq. S2 of pristine CsPbBr$_3$ at 4 K under a transverse magnetic field of 0.5 Tesla, after the initial spin imbalance generated by a test magnetic field. We find the fitted curve matches the calculated one perfectly after 0.2 ns, which gives spin lifetime $\tau_{s,i}$ and the Larmor precession frequency $\Omega$ through Eq. S2.

SII. COMPUTATIONAL DETAILS

The ground-state electronic structure, phonon, as well as electron-phonon and electron-impurity matrix elements are firstly calculated using Density Functional Theory (DFT), with relatively coarse $k$ and $q$ meshes in the plane-wave DFT code JDFTx[? ]. We use Perdew–Burke–Ernzerhof exchange-correlation functional[? ]. The structures are fully optimized and the lattice constants are 8.237, 8.514 and 11.870 Å. The phonon calculations employ $2 \times 2 \times 1$ supercells through finite difference calculations. We use Optimized Norm-Conserving Vanderbilt (ONCV) pseudopotentials[? ] with self-consistent spin-orbit coupling throughout, where we find convergence at a wavefunction kinetic energy cutoff of 48 Ry.

The e-i matrix $g^{i}$ between state $(k,n)$ and $(k',n')$ is

$$g^{i}_{kn,k'n'} = \langle kn| \Delta V^{i} |k'n'\rangle,$$

$$\Delta V^{i} = V^{i} - V^{0},$$

where $V^{i}$ is the potential of the impurity system and $V^{0}$ is the potential of the pristine system. $V^{i}$ is computed with SOC using a $2 \times 2 \times 1$ supercell with a neutral impurity. To speed up the supercell convergence, we used the potential alignment method developed in Ref. ? .

We then transform all quantities from plane wave basis to maximally localized Wannier function basis, and interpolate them to substantially finer $k$ and $q$ meshes[? ? ? ]. The Wannier interpolation approach fully accounts for polar terms in the e-ph matrix elements and phonon dispersion relations, using the approach developed by Verdi and Giustino[? ]. The Born effective charges and electronic dielectric constants are calculated from open-source code QuantumESPRESSO[? ]. The e-e scattering matrix is computed using the same method given in Ref. ? with the macroscopic static dielectric constant about 36 computed from density functional perturbation theory (DFPT)[? ] in QuantumESPRESSO. The fine $k$ and $q$ meshes are $48 \times 48 \times 32$ for simulations at 300 K and are finer at lower temperature, e.g., $180 \times 180 \times 120$ for simulations at 4 K. The computation of e-i and e-e matrix elements and the real-time dynamics simulations are done with the DMD code (Density-Matrix Dynamics), interfaced to JDFTx. The energy-conservation smearing parameter $\sigma$ is chosen to be comparable or smaller than $k_{B}T$ for each calculation.
SIII. THE BAND STRUCTURE AND PHONON DISPERSION

FIG. S2. (a) The band structure of CsPbBr$_3$ from DFT calculation with PBE functional and spin-orbit coupling (red) and from Wannierization (black), with the Fermi level being aligned to 0. (b) The band structure of CsPbBr$_3$ from DFT calculation with EV93PW91 functional. Phonon dispersion of CsPbBr$_3$ (c) without and (d) with considering LO-TO splitting with PBE functional. Our phonon dispersion is in good agreement with previous theoretical one reported in Ref. 7.

Figure S2a shows a direct band gap of CsPbBr$_3$ at $\Gamma$, suggesting that spin relaxation is important at $\Gamma$ where carriers occupy first. The perfect overlap between the DFT band structure and Wannier band structure implies good Wannierization quality. The band structure simulated using EV93PW91 functional is shown in Fig. S2b and gives a larger band gap than PBE in Fig. S2a.

By comparing the phonon dispersion of CsPbBr$_3$ at PBE without LO-TO splitting (Fig. S2c) to that with LO-TO splitting (Fig. S2d), we found that the long-range dipole potential field strongly splits the optical modes near 14 meV at $\Gamma$. This gives rise to $\sim$2 meV blueshift of the No. 57 optical mode within the 60 modes in total. The No. 57 (O57) and No. 58 (O58) optical modes were found to play significant roles in carrier relaxation. The corresponding discussion can be found from section “Analysis of spin-phonon relaxation” in the main text.
FIG. S3. Visualization of the CsPbBr$_3$ phonon modes (a)-(b) O57 and (c)-(d) O58 when $q = (0.001, 0, 0)$ Bohr$^{-1}$, (e)-(f) O57 and (g)-(h) O58 when $q = (0, 0.001, 0)$ Bohr$^{-1}$, and (i)-(j) O57 and (k)-(l) O58 when $q = (0, 0, 0.001)$ Bohr$^{-1}$. The red arrows represent the phonon displacement vectors.

In terms of the symmetry, bulk CsPbBr$_3$ belongs to $Pnma$ space group ($D_{2h}^{16}$). By visualizing the displacement patterns as shown in Fig. S3, O57 and O58 phonon modes transform as $B_{3g}$ and $B_{2g}$, respectively. And both of them are Raman-active based on symmetry.

SIV. THE BENCHMARK OF ORBITAL ANGULAR MOMENTUM L IMPLEMENTATION

|                     | This work | Theory 1 | Theory 2 | Exp. 1 |
|---------------------|-----------|----------|----------|--------|
| $L_{z,K,v-1}$       | 4.09      | 3.72     | 3.94     |        |
| $L_{z,K,v-1}$       | 4.30      | 3.93     | 4.10     |        |
| $L_{z,K,c}$         | 2.06      | 2.09     | 1.98     |        |
| $L_{z,K,c+1}$       | 1.84      | 1.87     | 1.76     |        |
| $g_A$               | -4.48     | -3.68    | -4.24    | -4.6   |
| $g_B$               | -4.50     | -3.70    | -4.36    | -4.3   |

TABLE S1. The benchmark of orbital angular momentum and $g$ factors of monolayer MoS$_2$. $L_{z,K,n}$ is the single-band orbital angular momentum along $z$ direction of band $n$ at high-symmetry $k$-point $K$, which is the diagonal element of $L_{z,K}$ matrix. $v$ and $c$ denote the highest valence and lowest conduction bands respectively. $g_A$ and $g_B$ are $g$-factor of A and B excitons respectively. The theoretical $g_A$ and $g_B$ shown here are computed without considering excitonic effects and $g_A = 2(L_{K,c+1} - L_{K,v})$ and $g_B = 2(L_{K,c} - L_{K,v-1})$ (see Ref. ?). Theory 1 and 2 are theoretical results from Ref. ? and ? respectively. Exp. 1 are experimental data from Ref. ?.

To verify our implementation of orbital angular momentum, we did benchmark calculations of single-band orbital angular momentum and $g$-factor of A and B excitons of monolayer MoS$_2$. We find that our results (Table S1) are in good agreement with previous theoretical and experimental results[? ? ?].
SV. $V_{xc}$-DEPENDENCE OF $g$-FACTOR AND ANOTHER $g$-FACTOR DEFINITION

The accurate prediction of $g$-factor requires accurate electronic structure as inputs, therefore we examine $g$-factors using DFT states from different exchange-correlation functionals ($V_{xc}$). In Fig. S4, we show $k$-dependent $g$-factor $\tilde{g}_k$ calculated using three different $V_{xc}$ - PBE, SCAN and EV93PW91. PBE as a GGA functional and SCAN as a meta-GGA functional were commonly employed in the DFT calculations. EV93PW91 was known to improve band gap values compared with local or semi-local functionals [1]. We found that EV93PW91 predicted a better band gap of about 1.42 eV (see the EV93PW91 band structure in Fig. S2(b)), compared with the PBE one with a band gap of 1.03 eV in Fig. S2(a), and the SCAN one with a value of 1.18 eV (the experimental one is at 2.36 eV [2]). EV93PW91 predicted the electron effective mass of about 0.27 $m_e$, improved over PBE at 0.22 $m_e$ and SCAN at 0.24 $m_e$ respectively, against the experimental one at 0.26 $m_e$ [3].

From Fig. S4, we find that for all $V_{xc}$, the calculated electron $\tilde{g}_k$ are larger than hole $\tilde{g}_k$ and the sums of electron and hole $\tilde{g}_k$ range from 1.85 to 2.4, in agreement with experiments [4, 5]. More importantly, for all $V_{xc}$, $\tilde{g}_k$ of electrons and holes decrease and increase with state energy respectively, the fluctuation of $\tilde{g}_k$ increases with the state energy and the $g$-factor fluctuation amplitudes $\Delta \tilde{g}$ are of the same order of magnitude.

However, both electron and hole $\tilde{g}_k$ are found sensitive to $V_{xc}$; in particular, the signs of hole $\tilde{g}_k$ are different among different $V_{xc}$. Overall, we find that the magnitudes of $g$-factors predicted by EV93PW91 are in the best agreement with experiments. EV93PW91 predicts electron $g$-factor $\sim 1.8$ and hole $\sim 0.5$ at $\Gamma$ respectively, close to experimental data [1] (1.69-2.06 for electrons and 0.65-0.85 for holes). On the other hand, both PBE [4] and SCAN [5] functionals overestimate electron $g$-factor and underestimate hole $g$-factor compared with experimental values [4, 5]. Furthermore, the anisotropy of hole $g$-factor along three crystal directions is found greater than that of electron, in agreement with experiments [5]. With EV93PW91, the theoretical anisotropy ratio $P$ of electron and hole $g$-factors at $\Gamma$ are 6% and 15% respectively, in reasonable agreement with experiments (10% for e and 13% for h) [5], where $P = |g_{\text{max}} - g_{\text{min}}|/g_{\text{max}} + g_{\text{min}}$ with $g_{\text{max}}$ ($g_{\text{min}}$) the maximum (minimum) value of $g$-factors among three directions.

The strong $V_{xc}$-dependence of $g$-factors indicate that accurate electronic structure is important for quantitative comparison of $g$-factor with experiments. Therefore, to reliably predict the $g$-factor values, we may need to employ a higher level of theory, such as the GW approximation [6, 7], to improve the electronic structure description and lessen such dependence on the choice of DFT $V_{xc}$. On the other hand, $T_2^*$ only depends on $\Delta \tilde{g}$, which are less sensitive to $V_{xc}$, e.g., $\Delta \tilde{g}$ by the SCAN functional [5] is $\sim 80\%$ of that by PBE. Moreover, the trends of $g$-factors and $\Delta \tilde{g}$ versus electronic energies are the same for different $V_{xc}$. Therefore, we expect that different $V_{xc}$ predict similar magnitudes of $T_2^*$ and the same trends of $T_2^*$ versus external conditions.

Below, we provide a more generate definition of $g$-factor and its fluctuation amplitude, which is more appropriate when spin directions (at different $k$) are not parallel to the direction of the applied $B$, and materials are highly
Generally speaking, except at some high-symmetry k-point, L and L + g0S may not be proportional to S. Since under finite B, the expectation value vectors of L + g0S must be parallel to B (in the first-order perturbation level), spin expectation value vectors may not be parallel to B. Therefore, it is helpful to define a vector of Larmor precession frequency whose magnitude is equal to the energy splitting,

\[ \overrightarrow{\Omega}_k (B) = \Delta E_k (B) \overrightarrow{S}_{k,h}^{\text{exp}} (\overrightarrow{B}), \]  

(S5)

\[ \overrightarrow{S}_{k,h}^{\text{exp}} (\overrightarrow{B}) = \frac{\overrightarrow{S}_{k,h}^{\text{exp}} (\overrightarrow{B})}{|\overrightarrow{S}_{k,h}^{\text{exp}} (\overrightarrow{B})|}, \]  

(S6)

where \( \overrightarrow{S}_{k,h}^{\text{exp}} (\overrightarrow{B}) \) is the spin expectation value vector.

With the distribution of \( \overrightarrow{\Omega}_k \), we can define a g-factor vector and a more appropriate g-factor fluctuation amplitude for spin dephasing.

With \( \overrightarrow{\Omega}_k \), we can define a g-factor vector (with \( C^{S \rightarrow J} \) defined in the main text) as

\[ \overrightarrow{g}^{\Omega} (\overrightarrow{B}) = C^{S \rightarrow J} \frac{\overrightarrow{\Omega}_k (B)}{\mu_B B}. \]  

(S7)

With \( \overrightarrow{g}^{\Omega} (\overrightarrow{\xi}), \overrightarrow{g}^{\Omega} (\overrightarrow{y}) \) and \( \overrightarrow{g}^{\Omega} (\overrightarrow{z}) \), we will obtain a g-factor tensor.

A more appropriate definition of g-factor fluctuation amplitude for spin dephasing requires the detailed knowledge of \( \overrightarrow{\Omega}_k \). Suppose the total excited or excess spin \( \overrightarrow{S}_{\text{tot}} \) is perpendicular to B, i.e., \( \overrightarrow{S}_{\text{tot}} \perp \overrightarrow{B} \), then without considering the EY spin relaxation, \( \tau_s \) will be mainly determined by \( \Delta \Omega_{\perp \overrightarrow{S}_{\text{tot}}} \) - the fluctuation amplitude of \( \overrightarrow{\Omega}_{\perp \overrightarrow{S}_{\text{tot}}} \), which is the component of \( \overrightarrow{\Omega} \) perpendicular to \( \overrightarrow{S}_{\text{tot}} \).

Suppose the unit vectors \( \hat{e}_1, \hat{e}_2 \) and \( \hat{e}_3 \) orthogonal among each other, then similar to Eq. 10 in the main text, we can define \( \Delta \Omega_{\perp \hat{e}_1} \) as

\[ \Delta \Omega_{\perp \hat{e}_1} = \sqrt{(\Delta \Omega_{\hat{e}_2})^2 + (\Delta \Omega_{\hat{e}_3})^2}, \]  

(S8)

\[ \Delta \Omega_{\hat{e}} = \frac{\sum_k (-f'_k) |\Omega_{k,\hat{e}} - \overrightarrow{\Omega}_{\hat{e}}|^2}{\sum_k (-f'_k)^2}, \]  

(S9)

\[ \overrightarrow{\Omega}_{\hat{e}} = \frac{\sum_k (-f'_k) \Omega_{k,\hat{e}}}{\sum_k (-f'_k)}, \]  

(S10)

where \( \Omega_{\hat{e}} \) is the \( \hat{e} \) component of \( \overrightarrow{\Omega} \). As \( \overrightarrow{S}_{\text{tot}} \) is approximated rotating about \( \overrightarrow{B} \), \( \overrightarrow{\Omega}_{\perp \overrightarrow{S}_{\text{tot}}} \) changes with time. Suppose the unit vectors \( \hat{e}_a \) and \( \hat{e}_b \) satisfy \( \hat{e}_a \perp \hat{e}_b, \hat{e}_a \perp \overrightarrow{B} \) and \( \hat{e}_b \perp \overrightarrow{B} \), we can define an effective fluctuation amplitude of \( \overrightarrow{\Omega} \) (B) as

\[ \Delta \Omega ((\overrightarrow{B})) = \sqrt{(\Delta \Omega_{\perp \hat{e}_a} / 2)^2 + (\Delta \Omega_{\perp \hat{e}_b} / 2)^2} \]

(S11)

\[ = \sqrt{(\Delta \Omega_{\hat{e}})^2 + \frac{1}{2} (\Delta \Omega_{\hat{e}_a})^2 + \frac{1}{2} (\Delta \Omega_{\hat{e}_b})^2}. \]

With \( \Delta \Omega ((\overrightarrow{B})) \), we can define a \( T \) and \( \mu_e \) dependent effective fluctuation amplitude of g-factor under B,

\[ \Delta g^{\Omega} (\overrightarrow{B}) = \frac{\Delta \Omega ((\overrightarrow{B}))}{\mu_B B}. \]  

(S12)

For CsPbBr₃, we find Eq. S12 predicts quite similar values to those by Eq. 10 in the main text (differences are not greater than 10%).
SVI. SPIN RELAXATION TIMES

FIG. S5. (a) Electron and (b) hole $\tau_s$ of pristine CsPbBr$_3$ as a function of $T$ at different carrier density $n_c$ including both electron-phonon and electron-electron scatterings. The brown triangle lines represent $\tau_s$ without electron-electron (w/o e-e) scatterings.

FIG. S6. (a) Electron and (b) hole $\tau_s$ of pristine CsPbBr$_3$ along $x$, $y$ and $z$ Cartesian directions with carrier density $n_c = 10^{18}$ cm$^{-3}$ as a function of temperature.

In Fig. S6, we show electron and hole $\tau_s$ of pristine CsPbBr$_3$ along $x$, $y$ and $z$ directions and we find both of them are nearly isotropic.
FIG. S7. Electron $\tau_s$ of CsPbBr$_3$ with different types of point defects/impurities. Both electron carrier density $n_e$ and impurity density $n_i$ are $10^{18}$ cm$^{-3}$. (a) With neutral Cs-derived impurities, where V$_{\text{Cs}}$ denotes Cs vacancy; Cs$_{\text{Br}}$ denotes Cs substitution of Br; Cs$_{\text{Pb}}$ denotes Cs substitution of Pb; Cs$_\text{i}$ denotes interstitial Cs doping. (b) With neutral Pb-derived impurities. (c) With neutral Br-derived impurities.

From Fig. S7, we find that the impurity effects are sensitive to the atomistic details of impurities, but all impurities studied here cannot affect $\tau_s$ at $T \geq 20$ K if impurity density $n_i$ is not extremely high (e.g. $< 10^{18}$ cm$^{-3}$).

SVII. CARRIER AND SPIN TRANSPORT PROPERTIES IN LOW DENSITY LIMIT

We calculate the electron mobility $\mu_e$ and the hole mobility $\mu_h$ by solving the linearized Boltzmann equation in relaxation-time approximation[? ? ? ?],

$$\mu_{e(h),i} = \frac{e}{n_{e(h)}VN} \sum_{k,n \in \text{CB(VB)}} \frac{df}{d\epsilon_e} \delta(\epsilon_{e(h)} v_{kn, i} \tau_{m, kn}),$$

(S13)

where $i = x, y, z$ for three dimensional systems. $N_k$ is the number of k points. $V$ is the unit cell volume. $n_e$ and $n_h$ are electron and hole density respectively. CB and VB denote conduction and valence bands, respectively. $f$ is Fermi-Dirac function. $\mu_F$ is the chemical potential. $v$ is the band velocity. $\tau_m$ is the momentum relaxation time. Using the Matthiessen’s rule, we have

$$\tau_{m, kn}^{-1} = \frac{1}{N_k} \sum_{k'} \left( \tau_{m, kn \rightarrow k'n'}^{-1} \right) \left( 1 - \cos \theta_{k'kn} \right),$$

(S15)

$$\tau_{m, kn \rightarrow k'n'}^{-1} = \frac{2\pi}{\hbar} \sum_{\lambda, \pm} |g_{k'kn, k'n'}|^2 (\epsilon_{k'kn} + 0.5 \mp (0.5 - f_{k'n})) \delta(\epsilon_{k'kn} - \epsilon_{kn} \mp \hbar \omega_{k'kn}),$$

(S16)

$$\tau_{m, kn \rightarrow k'n'}^{-1} = n_i V \frac{2\pi}{\hbar} \sum_{\lambda, \pm} |g_{k'kn, k'n'}|^2 \delta(\epsilon_{k'kn} - \epsilon_{kn}),$$

(S17)

$$\tau_{m, kn \rightarrow k'n'}^{-1} = \frac{2\pi}{\hbar} \sum_{k'_3 k'_4 n_4} \left[ |g_{k'3k'_4 n'_4}|^2 \delta_{k'3k'4} \right] \left[ f_{k'kn} f_{k'4n_4} (1 - f_{k'3n'}) + (1 - f_{k'kn}) f_{k'3n_3} (1 - f_{k'4n_4}) \right] \times \delta(\epsilon_{kn} + \epsilon_{k'_3n'_4} - \epsilon_{k'kn} - \epsilon_{k'4n_4}).$$

(S18)

$$\cos \theta_{k'kn} = \frac{\vec{v}_{k'kn} \cdot \vec{v}_{kn}}{|\vec{v}_{k'kn}| |\vec{v}_{kn}|},$$

(S19)
where $c$ represents $e-e$, $e-ph$, or $e-e$; $g^{k'-k,\lambda}_{kn}$ is the e-ph matrix element between state $(k',n')$ and state $(k,n)$ with phonon mode $\lambda$; and $g^{k'n',kn}_{k'n,n}$ is the e-i matrix element defined in Eq. S3 and computed with DFT supercells with neutral impurities. $n_{k',n',\lambda}$ is the phonon occupation number. $g_{k'k,n'n}$ is the e-e matrix element defined in Eq. A6 in Ref. ? . $f^{eq}_{kn}$ is the equilibrium occupation of electronic state $(k,n)$.

We compute spin diffusion length $l_s$ for $z$-direction spin transport and spin polarization using the relation $\tau_s = \frac{1}{D \tau_s}$, where $D$ is diffusion coefficient. $D$ can be estimated using the general form of Einstein relation $D = \mu_c n_c / \frac{d\mu}{dn_c}$, where $\mu_c$ is the free-carrier mobility, $\mu_{F,c}$ is the chemical potential, and $n_c$ is the carrier density.

**FIG. S8.** Calculated mobility $\mu_c$ (a) and spin diffusion length $l_s$ (b) of electrons of pristine CsPbBr$_3$ in low density limit as a function of temperature. “expt.” denotes experimental data from Ref. [? ].

Fig. S8 shows calculated mobility $\mu_c$ and spin diffusion length $l_s$ of electrons of pristine CsPbBr$_3$ in low density limit (here $n_c$ is taken as $10^{14}$ cm$^{-3}$), which set the upper bounds of $\mu_c$ and $l_s$. Considering that there are no impurities and the e-e scattering is not active in low density limit, only the e-ph scattering contributes here. From Fig. S8a and b, we find that both $\mu_c$ and $l_s$ increase fast with decreasing $T$ and can reach very high values at low $T$, e.g., $l_s$ can be as long as hundreds of $\mu$m at 4 K.

**SVIII. MAGNETIC-FIELD EFFECTS ON $\tau_s$ UNDER LOW $B$**

**FIG. S9.** The effects of transverse magnetic fields (perpendicular to spin direction) on electron $\tau_s$ of pristine CsPbBr$_3$ under $B \leq 1$ Tesla. Different solid lines denote $\tau_s$ at different electron carrier density. The estimated experimental carrier density is around $10^{18}$cm$^{-3}$ (corresponding to the black line here). The orange empty diamond denotes the experimental values, with dashed line as their linearly fitted values.
FIG. S10. Transient circularly-polarized photoinduced reflection in CsPbBr$_3$ single crystal excited at 405 nm measured at 4K on the (001) facet with $B$ along [010] orientation. (a) $B=0$ mT and (b) $B=400$ mT. The spin lifetime in (a) is measured after the ‘coherence artefact’ seen at $t=0$. The spin lifetime in (b) is measured from the decay of the quantum beatings of the photocarriers.