Spin-phonon relaxation in disparate materials from a universal \textit{ab initio} density matrix approach

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The design of new quantum materials with long-lived electron spin states requires a general theoretical formalism and computational technique to predict intrinsic spin relaxation times, but current methods require specialized approaches for each class of material and electronic structure. We present a new, universal first-principles methodology based on Lindbladian dynamics of density matrices to calculate the spin-phonon relaxation time ($\tau_s$) of solids with arbitrary spin mixing and crystal symmetry. In particular, this method describes contributions of the Elliott-Yafet (EY) and D'yakonov-Perel' (DP) mechanisms to spin relaxation, corresponding to systems with and without inversion symmetry, on an equal footing. Our \textit{ab initio} predictions are in excellent agreement with experimental data for a broad range of materials, including metals and semiconductors with inversion symmetry (silicon and iron), and materials without inversion symmetry (MoS$_2$ and MoSe$_2$). We find strong magnetic field dependence of electron and hole spin relaxation in MoS$_2$ and MoSe$_2$. As a function of temperature, we find the spin relaxation time ($\tau_s$) to be proportional to carrier/momentum relaxation time ($\tau_m$) in all cases, consistent with experiments but distinct from the commonly-quoted inverse relation for simplified models of the DP mechanism. We emphasize that first-principles spin-orbit coupling and electron-phonon scattering is crucial for general and accurate prediction of spin relaxation in solids.

I. INTRODUCTION

The manipulation of electron spins is of increasing interest in a wide-range of emerging technologies. The rapidly growing field of spintronics seeks to control spin as the unit of information instead of charge$^3$ in devices such as spin transistors$^{4,5}$. Quantum information technologies seek to utilize localized spin states in materials both as single-photon emitters and as spin-qubits for future integrated quantum computers$^6$. Both spintronics and quantum information applications therefore demand a quantitative understanding of spin dynamics and transport in metals and semiconductors. Recent advances in circularly-polarized pump-probe spectroscopy$^7$, spin injection and detection techniques$^8$, have enabled increasingly-detailed experimental measurement of spin dynamics in solid-state systems. However, a universal first-principles theoretical approach to predict spin dynamics, quantitatively interpret these experiments and design new materials has remained out of reach.

A key metric of useful spin dynamics is the spin relaxation time $\tau_s$.$^1$ For example, spin-based quantum information applications require $\tau_s$ exceeding milliseconds for reliable qubit operation. Consequently, accurate prediction of $\tau_s$ in general materials is an important milestone for first-principles design of quantum materials. Spin-spin, spin-phonon, and spin-impurity scatterings all contribute to spin relaxation, but spin-phonon scattering sets the intrinsic material limitation and is typically the dominant mechanism at room temperature$^9$. Furthermore, spin-phonon relaxation arises from a combination of spin-orbit coupling (SOC) and electron-phonon scattering, and is traditionally described by two mechanisms. First, the Elliott-Yafet (EY) mechanism involves spin-flip transitions between pairs of Kramers degenerate states due to SOC-based spin mixing of these states$^{10,11}$. Second, the D'yakonov-Perel' (DP) mechanism in systems with broken inversion symmetry involves electron spins precessing between scattering events due to the SOC-induced internal effective magnetic field$^{12}$.

Previous theoretical approaches have extensively investigated these two distinct mechanisms of intrinsic spin-phonon relaxation using model Hamiltonians in various materials$^{13-16}$. These methods require parametrization for each specific material, which needs extensive prior information about the material and specialized computational techniques, and often only studies one mechanism at a time. Furthermore, most of these approaches require the use of simplified formulae$^{10,12,13,16}$ and make approximations to the electronic structure (e.g. low spin mixing) or electron-phonon matrix elements$^{15}$. This limits the generality and reliability of these approaches for complex materials, particularly for the DP mechanism, where various empirical relations are widely employed to estimate $\tau_s$.$^{13,19,21}$ Sophisticated methods based on spin susceptibility$^{22}$ and time evolution of density matrix$^{15}$ also rely on suitably chosen model Hamiltonians with empirical scattering matrix elements. Therefore, while these methods provide some mechanistic insight, they do not serve as predictive tools of spin-relaxation time for
the design of new materials.

A general first-principles technique to predict spin-phonon relaxation in arbitrary materials is therefore urgently needed. Previous first-principles studies have addressed the EY mechanism in a few semiconductors and metals, requiring different techniques for each. These methods rely on defining a pseudo-spin that allows the use of Fermi’s golden rule (FGR) with only spin-flip transitions. However, this is only well-defined for cases with weak spin mixing such that eigenstates within each Kramers-degenerate pair can be chosen to have small spin-minority components, precluding the study of spin relaxation of states with strong spin-mixing, e.g. holes in silicon and noble metals. First-principles calculations have not yet addressed systems with such complex degeneracy structures, where the simple picture of spin-flip matrix elements in a FGR breaks down, or systems without inversion symmetry that do not exhibit Kramers degeneracy. Therefore, a more general first-principles technique without the material-specific simplifying assumptions of these previous approaches is now necessary.

In this work, we establish a new, accurate and unified first-principles technique for predicting spin relaxation time based on perturbative treatment of the Lindbladian dynamics of density matrices. Importantly, by covering previously disparate mechanisms (e.g. EY and DP) in a unified framework, this technique is applicable to all materials regardless of dimensionality, symmetry (especially inversion) and strength of spin mixing, which is critical for new material design. All SOC effects are included self-consistently (and non-perturbatively) in the ground-state eigensystem at the Density Functional Theory (DFT) level, and we predict $\tau_s$ through a universal rate expression without the need to invoke real-time dynamics.

We demonstrate the generality of our method by applying it to three distinct types of systems. First, we consider two materials with inversion symmetry and vastly different electronic structure: silicon, a non-magnetic semiconductor whose electron $\tau_s$ has been well studied experimentally and theoretically, and iron, a ferromagnetic metal. Beyond past first-principle studies that assume weak spin mixing and a simple spin flip mechanism, we also reliably predict the hole $\tau_s$ of silicon where spin mixing is strong.

More importantly, for the first time, we demonstrate first-principles calculations of $\tau_s$ for systems without inversion symmetry - MoS$_2$ and MoSe$_2$. These transition metal dichalcogenides (TMDs) exhibit extremely long-lived spin/valley polarization (over nanoseconds) with long valley-state persistence attributed to spin-locking effects. A fundamental understanding of spin/valley relaxation mechanisms is now required to utilize this degree of freedom for valleytronic computing. However, experimental techniques such as time-resolved Kerr rotation (TRKR) and photoluminescence (Hanle effect) measurements probe spin and valley dynamics in a coupled manner, based on their selection rules with circularly polarized light, making individual relaxation times difficult to determine. Our first-principles methods disentangle spin and valley relaxation times, and determine their underlying mechanisms in different TMDs.

Finally, we quantify the variation of relaxation times with external magnetic field, with TMDs as an initial example. This is important to understand as a path-way to tune material properties, and because spin relaxation measurements intrinsically involve magnetic fields. In this article, we first introduce our theoretical framework based on first-principles density matrix dynamics, and then show three prototypical examples of $\tau_s$ for the broad range of systems discussed above, in excellent agreement with available experimental data. By doing so, we establish the foundation for quantum dynamics of open systems from first-principles to facilitate the design of quantum materials.

II. THEORY AND COMPUTATIONAL METHOD

A. Density matrix dynamics formalism for spin relaxation time

The key to treating arbitrary state degeneracy and spin mixing for spin relaxation is to switch to an \textit{ab initio} density-matrix formalism, which goes beyond specific cases such as Kramer degeneracy or Rashba-split model Hamiltonians. Specifically, we seek to work with density matrices of electrons alone, treating its interactions with an environment consisting of a thermal bath of phonons. In general, tracing out the environmental degrees of freedom in a full quantum Liouville equation of the density matrix results in a quantum Lindblad equation. Specifically, for electron-phonon coupling based on the standard Born-Markov approximation that neglects memory effects in the environment, the Lindbladian dynamics in interaction picture reduces to

$$\frac{\partial \rho_{\alpha_1\alpha_2}}{\partial t} = \frac{2\pi}{\hbar N_q} \text{Re} \sum_{q_{\lambda\pm}\alpha'_1\alpha'_2} \left[ \left( I - \rho_{\alpha_1\alpha'_1} \right) (G^{q_{\lambda\pm}})_{\alpha_1'\alpha_2'} \rho_{\alpha_2'\alpha_2} (G^{q_{\lambda\pm}})_{\alpha_1\alpha_2} - \left( G^{q_{\lambda\pm}} \right)_{\alpha_1'\alpha_1} \left( I - \rho_{\alpha_2'\alpha_1} \right) (G^{q_{\lambda\pm}})_{\alpha_1\alpha_2} \rho_{\alpha_2'\alpha_2} \right] n_{q_{\lambda\pm}},$$

(1)
where $\alpha$ is a combined index labeling electron wavevector $k$ and band index $n$, $\lambda$ is mode index and $\pm$ corresponds to $q = \pm (k - k')$. $n_{q,\lambda}^\pm = n_{q,\lambda} + 0.5 \pm 0.5$ and $n_{q,\lambda}$ is phonon occupation. $G_{\alpha\alpha'}^{q,\lambda,\pm} = g_{\alpha\alpha'}^{q,\lambda,\pm} \delta^{1/2}(\epsilon_\alpha - \epsilon_{\alpha'}^\pm \pm \omega_{q,\lambda})$ is the electron-phonon matrix element including energy conservation, where $\omega_{q,\lambda}$ is the phonon frequency. As discussed in Ref [28] this specific form of the Lindbladian dynamics preserves positive definiteness of the density matrix which is critical for numerical stability.

The density-matrix formalism allows the computation of any observable such as number and spin density of carriers, and the inclusion of different relaxation mechanisms at disparate time scales from femtoseconds to nanoseconds, which forms the foundation of the general relaxation time approach we discuss below. Given an exponentially-relaxing measured quantity $O = Tr(\rho_p)$, where $\rho$ and $\rho_p$ are the observable operator and the density matrix respectively, we can define the relaxation rate $\Gamma_o$ and relaxation time $\tau_o = \Gamma_o^{-1}$ of quantity $O$ as

$$\frac{\partial (O - O^{eq})}{\partial t} = -\Gamma_o(O - O^{eq}),$$

where eq’ corresponds to the final equilibrium state.

The equilibrium density matrix in band space is $\langle \rho(q) \rangle_{eq}^{\lambda,n'\lambda',i,k} = f_{kn\lambda} \delta_{nn'}$, where $f_{kn\lambda}$ are the Fermi occupation factors of electrons in equilibrium. Writing the initial density matrix $\rho = \rho^{eq} + \delta \rho$, assuming a small perturbation $||\delta \rho|| \ll ||\rho^{eq}||$ and $k$-diagonal $\alpha$ and $\delta \rho$, the Lindblad dynamics expression (Eq. 1) and the definition (Eq. 2) yield

$$\Gamma_o = \frac{2\pi}{\hbar N_q Tr(\partial \rho/\partial\epsilon_f)} Tr_{\alpha} Re \sum_{kk'\lambda} \left[ (\partial \rho)_k G_{kk'}^{\alpha\lambda,\pm} \left( n_{q,\lambda} + I - f_{k'} \right) \right]_{\lambda\lambda'}^nk \left[ - (n_{q,\lambda} + f_k) G_{kk'}^{\alpha\lambda,\pm} (\partial \rho)_{k'} \right].$$

Here, the $G$ is exactly as defined above in Eq. 1 but separating the wave vector indices $(k, k')$ and writing it as a matrix in the space of band indices $(n, n')$ alone. Similarly, $\alpha$ and $\delta \rho$ are also matrices in the band space, $Tr_{\alpha}$ and $\epsilon_n$ are trace and Hermitian conjugate in band space, and $[\alpha, G]_{kk'} = \alpha_k G_{kk'} - G_{kk'} \alpha_{k'}$, written using matrices in band space.

Given an initial perturbation $\delta \rho$ and an observable $\alpha$, Eq. 3 can now compute the relaxation of expectation value $O$ from its initial value. Even for a specific observable like spin, several choices are possible for the initial perturbation corresponding directly to the experimental measurement scheme. Specifically for spin relaxation rate $\Gamma_{s,i}$, the observable is the spin matrix $S_i$ labeled by Cartesian directions $i = x, \ y, \ z$, and the initial perturbed state should contain a deviation of spin expectation value from equilibrium. The most general (experiment-agnostic) choice for preparing a spin polarization is to assume that all other degrees of freedom are in thermal equilibrium, which can be implemented using a test magnetic field $B$, as a Lagrange multiplier for implementing a spin polarization constraint.

Writing the initial perturbation Hamiltonian of $H_{SOC} = -2\mu_B B_i \cdot S_i/h$, where $\mu_B$ is the Bohr magneton, perturbation theory yields

$$\delta \rho_{k,mn} = \frac{-2\mu_B B_i}{h} f_{km} - f_{kn} S_i,_{k,mn}.$$  

For the systems we studied in this work, we notice that $S_i,_{k,mn} \approx 0$ when $\epsilon_{km} = \epsilon_{kn}$. Therefore, we have $\delta \rho \approx \frac{-2\mu_B B_i}{h} (\partial f / \partial \epsilon) S_i^{deg}$, where $(S_i^{deg})_{kmn} \equiv (S_i)_{kmn} \delta_{\epsilon_m \epsilon_n}$. $S_i^{deg}$ is the degenerate-subspace projection of $S_i$. For this choice, we can simplify Eq. 3 to the Fermi Golden rule-like expression,

$$\Gamma_{s,i} = \frac{2\pi}{\hbar N_i N_k B_i T \chi_{s,i}} \sum_{\lambda,\lambda',nn'} \left\{ \left| \left[ S_i^{deg} \right]_{\lambda\lambda'} \Delta n_{k,mn} \right|_{\lambda\lambda'}^n \left( \epsilon_{km} - \epsilon_{kn} - \omega_{q,\lambda} \right) f_{kn} \left( 1 - f_{kn} \right) n_{q,\lambda} \right\},$$

where $\chi_{s,i} = Tr_{\alpha} S_i (-\partial f / \partial \epsilon) S_i^{deg}/N_k$. Note that the test field $B_i$ etc. drops out of the final expression and only serves to select the direction of the perturbation in the high-dimensional space of density matrices. Without SOC, $S_i^{deg} = S_i$ commutes with $g$, leading to $\Gamma_{s,i} = 0$ as expected. If $S_i^{deg}$ is diagonal, $\left[ S_i^{deg} \right]_{\lambda\lambda'}$ reduces to $\Delta S_i,_{kkn',n'} \left( g_{kkn',n'}^{-} \right)$, where $\Delta S_i,_{kkn',n'} \equiv S_i,_{kn} - S_i,_{k'n'}$ is the change in (diagonal) spin expectation value for a
pair of states. Therefore, in this limit, Eq. 5 reduces to transitions between pairs of states, each contributing proportionally to the square of the corresponding spin change.

See Supplementary Information (SI) Sec. I and II for detailed derivations of the above equations. As we show in SI, Eq. 5 can be reduced to previous formulae with spin-flip matrix elements in Kramers degenerate subspaces for systems with inversion symmetry and weak spin mixing, such as conduction electron spin relaxation in bulk Si, similar to Ref. [23]. However, Eq. 5 is much more general, applicable for systems with arbitrary degeneracy and crystal symmetry as we will discuss later. Additionally, the overall framework can also be extended to other observables and can be made to correspond to specific measurement techniques that prepare a different initial density matrix e.g. a circularly-polarized pump pulse.

Finally, note that in our first-principles method, all SOC induced effects (such as the Rashba/Dresselhaus effects) are self-consistently included in the ground-state eigensystem or the unperturbed Hamiltonian $H_0$. This is essential to allow us to simulate $\tau_s$ by a single rate calculation when there is broken inversion symmetry. On the other hand, if SOC does not enter into $H_0$, as in previous work with model Hamiltonians, it must be treated as a separate term that provides an internal” effective magnetic field $H_{eff}$. Consequently, those approaches require a coherent part of the time evolution to describe the fast spin precession induced by this effective magnetic field, which require explicit real-time dynamics simulations even to capture spin relaxation, going beyond a simple exponential decay as in Eq. 2. Using fully self-consistent SOC in a first-principles method is therefore critical to avoid this system-specific complexity and arrive at the universal approach outlined above.

B. Computational details

All simulations are performed by the open-source plane-wave code - JDFTx [27] using pseudopotential method, except that the Born effective charges and dielectric constants are obtained from open-source code QuantumESPRESSO[28]. We firstly carry out electron structure, phonon and electron-phonon matrix elements calculations in DFT using Perdew-Burke-Ernzerhof exchange-correlation functional [49]. We use use pseudocells of size $7 \times 7 \times 7$, $4 \times 4 \times 4$, $6 \times 6 \times 1$, $6 \times 6 \times 1$ for silicon, BCC iron and monolayer MoS$_2$ and MoSe$_2$, respectively, which have shown reasonable convergence for each system (less than 20% error bar in the final spin relaxation estimates). SOC is included through the use of the fully-relativistic pseudopotentials [50-53]. For monolayer MoS$_2$ and MoSe$_2$, the Coulomb truncation technique is employed to accelerate convergence with vacuum

sizes [54].

We then transform all quantities from plane wave to maximally localized Wannier function basis [55] and interpolate them [56,57] to substantially finer k and q meshes (with $>3 \times 10^5$ total points) for lifetime calculations. Statistical errors computed using different random samplings of k-points are found to be negligible (< 1 %) for all lifetime calculations except at $T < 20$ K (error bars shown on corresponding results). This Wannier interpolation approach fully accounts for polar terms in the electron-phonon matrix elements and phonon dispersion relations using the approaches of Ref. [58] and [59] for the 3D and 2D cases respectively.

III. RESULTS AND DISCUSSIONS

A. Temperature-dependent $\tau_s$ of systems with inversion symmetry.

We first present results for systems with inversion symmetry (such as bulk Si and Fe) traditionally described by a Elliot-Yafet spin-flip” mechanism. Fig. 1(a) shows that our predictions of electron spin relaxation time ($\tau_s$) of Si as a function of temperature are in excellent agreement with experimental measurements [30,61]. Note that previous first-principles calculations [23] approximated spin-flip electron-phonon matrix elements from pseudospin wave-function overlap and spin-conserving electron-phonon matrix element, effectively assuming that the scattering potential varies slowly on the scale of a unit cell [22], we make no such approximation in our direct first-principles approach. Importantly, this allows us to go beyond the doubly-degenerate Kramers degenerate case of conduction electrons in Si. In contrast, holes in Si exhibit strong spin mixing with spin-2/3 character and spin expectation values no longer close to $\hbar/2$. Fig. 1(b) shows our predictions for the hole spin relaxation time which is much shorter than the electron case as a result of the strong mixing (770 fs for holes compared to 7 ns for electrons at 300 K) and is much closer to the momentum relaxation time. Additionally, Fig. 1(d) shows that the change in spin expectation values ($\Delta s$) per scattering event has a broad distribution for holes in Si, indicating that they cannot be described purely by spin-flip transitions, while conduction electrons in Si predominantly exhibit spin-flip transitions with $\Delta s = 1$.

We next consider an example of a ferromagnetic metal, iron, which exhibits a complex band structure not amenable for model Hamiltonian approaches. Previous first-principles calculations for ferromagnets employ empirical Elliott relation [32,33] or FGR formulae with spin-flip matrix elements specifically developed for metals or ferromagnets [24]. Here, we apply exactly the same technique used for the silicon calculations above and predict spin relaxation times in iron in excellent agreement with experimental measurements [51] (Fig. 1(c)). Our Wannier interpolation also enables systematic and efficient Bril-
Figure 1. Spin ($\tau_s$) and momentum ($\tau_m$) relaxation time predictions for two materials with inversion symmetry: (a) electrons in $n$-Si with carrier concentration $7.8 \times 10^{15}$ cm$^{-3}$ (compared to experiment[30,60]), (b) holes in $p$-Si with carrier concentration $1.3 \times 10^{15}$ cm$^{-3}$, and (c) iron (compared to experiment[61]). (d) Cumulative contributions to spin relaxation by change in spin, $\Delta s$, per scattering event: electrons in Si exhibit spin flips with all contributions at $\Delta s = 1$, whereas holes in Si and electrons in iron exhibit a broad distribution in $\Delta s$.

B. Electron and hole $\tau_s$ and the intravalley and intervalley contributions of MoS$_2$ and MoSe$_2$.

Next we investigate spin relaxation $\tau_s$ of systems without inversion symmetry from first-principles, using two TMD systems - monolayer MoS$_2$ and MoSe$_2$ as prototypical examples. In both systems, valence and conduction band edges at K and K’ valleys exhibit relatively large SOC band splitting, with nearly perfect out-of-plane spin polarization. Time-reversal symmetry further enforces opposite spin directions for the band-edge states at K and K’. Previous studies using Model Hamiltonians consider the DP mechanism to dominate spin relaxation in these materials[14,46], but in our first-principles approach, we do not need to a priori restrict our calculations to EY or DP limits.

In Fig. 2, we show the out-of-plane spin ($\tau_s$) and carrier ($\tau_m$) relaxation time of conduction electrons in two monolayer TMDs as a function of temperature, along with their intervalley/intravalley contributions and experimental values. First, the overall agreement between our calculations and previous experiments by ultrafast pump-probe spectroscopy is excellent[32,39,65]. Note that ultrafast measurements of TMDs obtain coupled dynamics of spin and valley polarizations according to the selection rules with circularly-polarized light, necessitating additional analysis to extract $\tau_s$, e.g., a phenomenologi-
Figure 2. Calculated spin ($\tau_s$) and momentum ($\tau_m$) relaxation times of conduction electrons of (a) MoS$_2$ and (b) MoSe$_2$ with carrier concentrations of $5.2 \times 10^{12}$cm$^{-2}$ and $5.0 \times 10^{11}$cm$^{-2}$ respectively (compared to experiment$^{32, 39, 65}$). Intra" and inter" denote intravalley (within K or K') and intervalley (between K and K') scattering contributions to the relaxation times; intravalley processes dominate spin relaxation at and below room temperature.

TABLE I: Percentage contributions of selected phonon modes to spin relaxation time ($\tau_s$) of conduction electrons of MoS$_2$ and MoSe$_2$. ZA, E' LA and LO respectively represent out-of-plane acoustic (flexural) mode, two lower-frequency in-plane optical modes, longitudinal acoustic and longitudinal optical phonon modes. (See phonon band structures in Supplementary Fig. S4).

| System | T (K) | $B_x$ (T) | Modes and their contributions |
|--------|------|-----|-----------------------------|
| MoS$_2$ | 300 | 0 | ZA(17%), 1st E'(21%), 2nd E'' (54%) |
| MoSe$_2$ | 300 | 0 | ZA(19%), 1st E' (31%), 2nd E'' (42%) |
| MoS$_2$ | 150 | 0 | ZA(49%), 1st E'(24%), 2nd E'' (27%) |
| MoS$_2$ | 300 | 1 | LA(50%), LO(24%) |

cal model fit to experimental curves in Ref. $^{32}$. On the other hand, our first-principles method simulates $\tau_s$ directly without model or input parameters. This provides additional confidence in the experimental procedures of extracting $\tau_s$, and lends further insights into different scattering contributions in the dynamical processes as we show below. Moreover, special care is necessary when comparing with certain low temperature measurements with lightly doped samples, which access spin relaxation of excitons rather than individual free carriers, as discussed in Ref. $^{38, 66}$; we focus here on spin relaxation of free carriers.

Next, comparing the relative contributions of intervalley and intravalley scattering for spin relaxation time, we find that the intravalley process dominates spin relaxation of conduction electrons in both TMDs: the intravalley-only spin relaxation time (black squares) in Fig. 2 is nearly identical with the net spin relaxation time (red circles), while the intervalley contribution alone (blue triangles) is consistently more than an order of magnitude higher in relaxation time (lower in rate). Further more, with decreasing temperature, the relative contribution of the intervalley process decreases because the minimum phonon energies for wave vectors connecting the two valleys exceed 20 meV, and the corresponding phonon occupations become negligible at temperatures far below 300 K.

Previous theoretical studies of MoS$_2$ with model Hamiltonians$^{46}$ obtained (out-of-plane) $\tau_s$ two orders of magnitude higher than our predictions which agree with experimental data$^{32}$. Such significant deviations are possibly because of the approximate treatments of electronic structure and electron-phonon coupling in their theoretical model. For instance, MoS$_2$ exhibits band-crossings within 20 meV of the CBM that have a large impact on $\tau_s$ for electrons in our predictions, which is missed completely in the model Hamiltonian study. In addition, our first-principle calculations also treat all phonon modes on an equal footing. Table I shows that the relative contributions of each phonon mode to $\tau_s$ varies strongly with temperature and magnetic field conditions, while model
Figure 3. Predicted spin ($\tau_s$) and momentum ($\tau_m$) relaxation times of holes in (a) MoS$_2$ and (b) MoSe$_2$ in the low carrier concentration limit ($<10^{11}$ cm$^{-2}$). In contrast to the electron case, the intervalley process dominates spin relaxation at low temperature in MoS$_2$ and at all temperatures in MoSe$_2$.

Hole spin relaxation in MoS$_2$ and MoSe$_2$ has not been previously investigated in detail theoretically. Fig. 3 presents our predictions of hole $\tau_s$ and $\tau_m$ in the two TMDs, indicating that hole $\tau_s$ is much longer than that for electrons at all temperatures, exceeding 1 ns below 100 K. In contrast to the electron case, the intervalley process is relatively much more important and dominates spin relaxation at low temperature in MoS$_2$ and at all temperatures in MoSe$_2$. This is because large SOC splitting at the valence band maximum makes the intravalley transition between two valence bands nearly impossible based on energy conservation in the electron-phonon scattering process. Experimental measurements also observe long spin relaxation times dominated by intervalley scattering in tungsten dichalcogenides which may facilitate applications in spin- and valley-tronic devices.

Finally, for both electrons and holes in MoS$_2$ and MoSe$_2$, we observe that $\tau_s$ is approximately proportional to carrier relaxation time $\tau_m$ and both decrease with increasing temperature, which is expected because both scattering rates ($\tau_s^{-1}$ and $\tau_m^{-1}$) are proportional to phonon occupation factors. This proportionality is also consistent with experimental observations (Fig. 2), but at odds with the inverse-proportional relation in commonly-used empirical formulae for the DP contribution. These empirical formulae were proposed to understand spin relaxation in specific materials at certain conditions, where other scattering mechanisms may dominate over electron-phonon scattering, and they may therefore not correctly describe spin relaxation processes dominated by electron-phonon scattering in TMDs.

Figure 4. Variation of spin relaxation time ($\tau_s$) with in-plane magnetic field for conduction electrons in MoS$_2$ and MoSe$_2$.

C. Magnetic-field dependence of $\tau_s$.

External magnetic fields are an inherent component of spin dynamics measurements and systems with broken inversion symmetry in particular may strongly respond to magnetic fields, as discussed in the introduction. We therefore investigate the effects of an external field $\vec{B}$ on $\tau_s$ by introducing a Zeeman term ($g_s\mu_B/B\cdot\vec{S}$) to the electronic Hamiltonian interpolated using Wannier functions (approximating $g_s \approx 2$), just prior to computing $\tau_s$ with Eq. 5. Fig. 4 shows that the out-of-plane $\tau_s$ of conduction electrons strongly decreases with increasing in-plane magnetic field $B_x$, in agreement with experimental work on MoS$_2$ and in general consistency with previous theoretical studies of $\tau_s$ for systems with broken inversion symmetry.

This strong magnetic field response has a simple intu-
itive explanation: in TMDs, the spin splitting of bands can be considered as the result of the internal effective magnetic field \( B_{so} \hat{z} \) due to broken inversion symmetry. Applying a finite \( B_z \) perpendicular to \( B_{so} \hat{z} \) will cause large spin mixing and increase the spin-flip transition probability. As spin relaxation rate is nearly proportional to this probability in TMDs, spin relaxation time \( \tau_s \) is then strongly reduced. The degree of reduction depends on the detailed electronic structure of MoS\(_2\) and MoSe\(_2\) as shown in SI Fig. S2 and S3: states closer to the band crossing are more sensitive to \( B_z \), and MoS\(_2\) exhibits a stronger \( B_z \) dependence because this band crossing is closer to the CBM in MoS\(_2\) than in MoSe\(_2\).

Hole spin relaxation in MoS\(_2\) and MoSe\(_2\) (not shown), on the other hand, exhibits very weak dependence on \( B_z \) because of the large band splitting and high internal effective magnetic field \( B_{so} \) for valence band-edge states compared to those near the conduction band minimum. This insensitivity of hole \( \tau_s \) to magnetic fields is also consistent with experimental studies of hole \( \tau_s \) in WS\(_2\) \(^{13}\) and WSe\(_2\) \(^{20}\).

Finally, out-of-plane magnetic field \( B_z \) has a negligible effect on spin relaxation for TMDs (not shown), unlike the in-plane magnetic field \( B_x \) or \( B_y \). This is because electronic states around band edges are already polarized along the out-of-plane direction under a strong internal \( B_{so} \hat{z} \). High experimental external magnetic fields \( \sim 1 \) Tesla are relatively weak in contrast and only slightly change the spin polarization of the states, rather than introducing a spin mixing that leads to spin relaxation.

**IV. OUTLOOK**

In summary, we have demonstrated an accurate and universal first-principles method for predicting spin relaxation time of arbitrary materials, regardless of electronic structure, strength of spin mixing and crystal symmetry (especially with/without inversion symmetry). Our work goes far beyond previous first-principles techniques based on a specialized Fermi’s golden rule with spin-flip transitions and provides a pathway to an intuitive understanding of spin relaxation with arbitrary spin mixing. In TMD monolayer materials, we clarify the roles of intravalley and intervalley processes, additionally resolved by phonon modes, in electron and hole spin relaxation. We predict long-lived spin polarization from resident carriers of MoS\(_2\) and MoSe\(_2\) and show their strong sensitivity of electron spin relaxation to in-plane magnetic fields.

The predictive power of first-principles calculations is crucial for providing fundamental understanding of spin relaxation in new materials. The same technique can be applied to predict spin relaxation in realistic materials with or without defects useful for quantum technologies, wherever spin relaxation is dominated by electron-phonon scattering. The extension of this technique to include electron-impurity scattering is relatively straightforward \(^{22}\) while electron-electron scattering is additionally challenging \(^{21,24}\). Finally, a robust understanding of ultrafast experiments may require simulation of real-time dynamics to capture initial state effects, probe wavelength effects and beyond-single-exponential decay dynamics, which is a natural next step within the general Lindbladian density-matrix formalism presented here.

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