Giant Spin Lifetime Anisotropy and Spin-Valley Locking in Silicene and Germanene from First-Principles Density-Matrix Dynamics

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Abstract

Through First-Principles real-time Density-Matrix (FPDM) dynamics simulations, we investigate spin relaxation due to electron-phonon and electron-impurity scatterings with spin-orbit coupling in two-dimensional Dirac materials - silicene and germanene, at finite temperatures and under external fields. We discussed the applicability of conventional descriptions of spin relaxation mechanisms by Elliott-Yafet (EY) and D’yakonov-Perel’ (DP) compared to our FPDM method, which is determined by a complex interplay of intrinsic spin-orbit coupling, external fields, and electron-phonon coupling strength, beyond crystal symmetry. For example, the electric field dependence of spin relaxation time is close to DP mechanism for silicene at room temperature, but rather similar to EY mechanism for germanene. Due to its stronger spin-orbit coupling strength and buckled structure in sharp contrast to graphene, germanene has a giant spin lifetime anisotropy and spin valley locking effect under nonzero $E_z$ and relatively low temperature. More importantly, germanene has extremely long spin lifetime (∼100 ns at 50 K) and ultrahigh carrier mobility, which makes it advantageous for spin-valleytronic applications.

Introduction

Shortly after the discovery of graphene, significant advances have been made in the field of spintronics, exploiting spin transport instead of charge transport, with much less dissipation and unprecedented potentials for low-power electronics. Several properties are key parameters for optimizing spin transport, such as long spin lifetime and diffusion length, high electronic mobility, spin-valley locking effect. Long spin lifetime and diffusion length ensure robust spin state during propagation in a device. The spin-valley locking effect is valuable for the emerging field of research - ”valleytronics”, which utilizes the valley-pseudospin degree of freedom as basic unit for quantum information technology.

Graphene is a very promising spintronic material in particular, with the extremely high electronic mobility and the longest known spin...
diffusion length at room temperature. However, due to its weak spin-orbit coupling (SOC), spin-valley locking effect may be realized only through external effects, e.g., through proximity effect - by interfacing with large SOC materials such as transition metal dichalcogenides (TMDs). Other 2D materials, including TMDs, have also shown exciting properties for spin-/valleytronics. For instance, in Ref. [10], the ultralong spin/valley lifetime is observed (e.g. 2 µs in p-type monolayer WSe$_2$ at 5 K) and the spin lifetime is insensitive to in-plane magnetic fields, which is a signature of the spin-valley locking effects. However, in general, TMDs have much lower electric mobility than graphene, which is not ideal for electronic device applications.

As the counterparts of graphene, silicene and germanene have attracted significant attention throughout a decade due to their resemblance and distinction from graphene [11,12]. They possess several remarkable properties, including gate-tunable carrier concentration, high electric mobility [13–17] (Fig. S8), quantum spin hall effects [20,21], etc. Moreover, due to the buckled geometry, their SOC strength is highly enhanced and they will also have the advantages of tunable band structures by applying perpendicular electric fields $E_z$ and high spin polarizations, which are promising for spintronic applications [14]. Their electronic structure under finite $E_z$ has similarity to those of TMDs: the signs of spins in $K$ and $K'$ valleys being opposite which is imposed by time-reversal symmetry, band splittings induced by SOC and highly polarized states. Therefore, silicene and germanene can combine the advantages of both graphene and TMDs but avoid some shortcomings such as limited spin lifetimes ($\leq$ tens of ns) in graphene samples [22-23] and the absence of spin-valley locking in graphene, and low mobilities in TMDs [11,12].

Despite of their promising properties, the potential for spin-based information technologies by silicene and germanene has yet to be demonstrated. Understanding spin dynamics and transport in materials is of key importance for spintronics and spin-based quantum information science, and one key metric of useful spin dynamics is spin lifetime $\tau_s$. Compared with graphene, of which $\tau_s$ has been extensively studied experimentally and theoretically [22-24], $\tau_s$ of silicene and germanene have not been measured and the existing few theoretical studies were done based on relatively simple models [27,28], which do not include realistic interactions with phonons and impurities. Recently we developed a First-Principles Density-Matrix (FPDM) approach with quantum descriptions of scattering processes between electron-phonon (e-ph), electron-impurities (e-i) and electron-electron, to simulate spin-orbit mediated spin dynamics in general solid-state systems with arbitrary symmetry [29,30]. By employing this new method, we will be able to predict $\tau_s$ of silicene and germanene at finite temperatures with realistic interactions with environment without introducing any simplified model or empirical parameters, for ps to µs timescale simulation.

Results and discussions

Electronic structure. We first show electronic quantities of silicene and germanene under different $E_z$, which are closely related to spin dynamics and essential for understanding spin relaxation mechanisms.

Fig. 1(a) describes a schematic picture of band structures under $E_z$. DFT results of band gaps and the average of band splittings $\langle \Delta \rangle$ between two conduction/valence bands (broken Kramers’ degeneracy under $E_z$ field) are shown in Fig. 1(c). ‘$\langle \rangle$’ represents taking average of electronic quantity $A$ by $\langle A \rangle = \sum_{kn} f'(\epsilon_{kn}) A_{kn}/\sum_{kn} f'(\epsilon_{kn})$, where $f'$ is the derivative of Fermi-Dirac distribution function, and $k$ and $n$ are k-point and band indices respectively. At $E_z = 0$, due to time-reversal and inversion symmetries, every two bands form a Kramers degenerate pair [11]. A finite $E_z$ splits a Kramers pair into spin-up and spin-down bands due to broken inversion symmetry and the splitting increases with $E_z$ (see Fig. 1(c)). As the earlier model Hamiltonian study presented, the phase transition from topological insulators to band insulators happens at the critical electric field $E_{cr}$ with the schematic band struc-
Figure 1: Electronic quantities of silicene and germanene under different perpendicular electric field ($E_z$). (a) The schematic diagrams of band structures of silicene and germanene under different $E_z$ (see calculated band structures in Fig. S3-S5), where $E_{cr}$ is the critical electric field leading to zero band gap. (b) The schematic diagrams of internal magnetic fields $B^{in}$ (blue arrows) at a Fermi circle near one Dirac cone of planar silicene, (buckled) silicene, (buckled) germanene induced by breaking inversion symmetry under finite $E_z$. $B^{in}_{kn} = 2\Delta_{kn} S^{exp}_{kn} / (g_e \mu_B)$, where $k$ and $n$ are k-point and band indices, respectively. $g_e \mu_B$ is the electron spin gyromagnetic ratio. $\Delta_{kn}$ is energy difference between two conduction (valence) bands when $n$ is a conduction (valence) band. $S^{exp}$ is a vector and $S^{exp} \equiv (S_x^{exp}, S_y^{exp}, S_z^{exp})$, where $S_i^{exp}$ is spin expectation value along direction $i$ and is the diagonal element of spin matrix $s_i$ in Bloch basis. (c) Band gaps (black lines) and the averaged band splitting energies ($\Delta$) (red lines) between two conduction/valence bands. (d) The averaged out-of-plane ($B^{in}_{z}$) and in-plane internal magnetic fields ($B^{in}_{x}$). Throughout this work, $\langle A \rangle$ means the average of electronic quantity $A$ and $\langle A \rangle = \sum_{kn} f'(\varepsilon_{kn}) A_{kn} / \sum_{kn} f'(\varepsilon_{kn})$. $f'$ is the derivative of Fermi-Dirac distribution function. In this figure, for averaging, $T = 300$ K and chemical potential $\mu$ is set in the middle of the band gap.

Based on our DFT calculations, the band gaps close in silicene and germanene (black solid and dashed lines in Fig. 1(c)) at 0.2 and 2.5 V/nm respectively, and the gaps open again above $E_{cr}$.

The band splittings between spin-up and down under a finite $E_z$ are effectively induced by $k$- and band-dependent “internal” magnetic fields $B^{in}$, which are SOC fields induced by broken inversion symmetry. $B^{in}$ is defined as $2\Delta_{kn} S^{exp}_{kn} / (g_e \mu_B)$, $g_e \mu_B$ is the electron spin gyromagnetic ratio. $S^{exp} \equiv (S_x^{exp}, S_y^{exp}, S_z^{exp})$, where $S_i^{exp}$ is spin expectation value along direction $i$ and is the diagonal element of spin matrix $s_i$ in Bloch basis.

In Fig. 1(b), we depict schematic diagrams of $B^{in}$ (blue arrows) on a Fermi circle near one Dirac cone of planar silicene, buckled silicene, and buckled germanene induced by finite $E_z$. In planar silicene, $B^{in}$ is purely in-plane, known as Rashba Spin-Orbit fields $B^{in}_R$. $B^{in}$ in buckled silicene is analogous to an admixture of $B^{in}_R$ and out-of-plane field $B^{in}_z$, because buckled geometry results in the presence of $B^{in}_z$. Different from silicene, $B^{in}$ in buckled germanene is nearly fully out-of-plane. This indicates that stronger intrinsic SOC in germanene significantly increases out-of-plane $B^{in}_z$ and, as a result, the proportion of in-plane component diminishes. We examine the averaged $B^{in}$ along $z$, $\langle B^{in}_z \rangle$, and along $x$, $\langle B^{in}_x \rangle$, under $E_z$ shown in Fig. 1(d). While $\langle B^{in}_z \rangle$ for silicene and germanene increase slowly with similar values, $\langle B^{in}_x \rangle$ for germanene due to stronger intrinsic SOC, rises much more rapidly than that for silicene as a function of $E_z$. $B^{in}$ and its anisotropy between $z$ and $x$ are very important for spin relaxation.

**Spin relaxation under finite $E_z$.** Spin lifetime, and even spin relaxation mechanism, can be tuned by applying electric fields. Under-
standing the effect of electric field is critical for the control and manipulation of spin relaxation. We start our theoretical studies of spin relaxation from its electric field dependence.

As we perform FPDM calculations of spin lifetimes in this work, it is important to understand the connection and distinction between FPDM method and previous theoretical models. Previously, spin relaxation mechanisms are often analyzed based on phenomenological models, such as Elliott–Yafet (EY) and D’yakonov-Perel’ (DP) mechanisms. EY represents the spin relaxation pathway due to spin-flip scattering. DP is activated when inversion symmetry is broken which results in random spin precession between adjacent scattering events. We denote their corresponding spin lifetime with \( \tau^E \) and \( \tau^D \) respectively. They are often approximated by some simplified relations: (i) \( (\tau^E)^{-1} \approx 4 \langle b^2 \rangle \langle \tau_p^{-1} \rangle \) (EY relation) along direction \( i \), where \( \tau_p \) is carrier lifetime. \( b_i^2 = 1 - 25 \exp^v \) is the degree of mixture of spin-up and spin-down states, so called “spin mixing”\(^{[31]}\), and is calculated at \( E_z = 0 \). (ii) \( (\tau^D)^{-1} \approx \langle \tau_p^{-1} \rangle (\Omega^2 - \Omega_i^2) \) (DP relation), where \( \Omega_{ii} = g_e \mu_B B_{ii}^\text{in} \) is Larmor precession frequency\(^{[31]}\) with \( B_{ii}^\text{in} \) defined earlier. Another qualitative estimation of the total spin relaxation rate by taking into account both mechanisms is using\(^{[30]}\) \( (\tau^E+D)^{-1} = (\tau^E)^{-1} + (\tau^D)^{-1} \). In the following, we will compare FPDM calculations and these phenomenological models with first-principles input parameters including \( \tau_p \), \( b_i^2 \) and \( \Omega_i \).

We first investigate out-of-plane and in-plane spin lifetime \( \tau_{s,z} \) and \( \tau_{s,x} \), respectively, and their anisotropy \( (\tau_{s,z}/\tau_{s,x}) \) at \( E_z = 0 \) and 300K. From Fig.2(a) and (b), we find that (i) \( \tau_{s,z} \) and \( \tau_{s,x} \) of silicene are much longer than germanene; (ii) large anisotropy (10-100) of \( \tau_s \) is observed for both materials, e.g., 47 and 14 for silicene and germanene at zero \( E_z \) respectively, much greater than 0.5 for graphene\(^{[32,33]}\). Both phenomena may be qualitatively understood based on EY relation (typically dominant in inversion symmetric systems) as discussed in the following. The comparison between FPDM calculations and EY relation with first-principles inputs is shown in Fig.2(c) and (d), and they give the same order of magnitude of spin lifetime. Roughly speaking, the larger spin lifetime of silicene is mainly from the smaller spin mixing \( b_i^2 \) compared with germanene based on their intrinsic SOC strength. While the large spin anisotropy for both systems is a result of large ratio of \( b_{zz}^2/b_{xx}^2 \) (Fig. S6(a)).

We then discuss \( E_z \) dependence of spin relaxation. From Fig.2(a) and (b), \( \tau_{s,x} \) of silicene and germanene rapidly reduces with increasing \( E_z \). This trend can be qualitatively understood as follows. Finite \( E_z \) breaks inversion symmetry and splits Kramers degeneracy. This induces \( B_{ii}^\text{in} \) with a rapidly increased \( z \) component as shown in Fig. (d), and thus leads to fast in-plane spin relaxation (perpendicular to \( B_{ii}^\text{in} \)) and reduces in-plane spin lifetime \( \tau_{s,x} \).

Unlike \( \tau_{s,x} \), out-of-plane spin lifetime \( \tau_{s,z} \) of germanene is insensitive to \( E_z \) in Fig. 2(c) although \( \tau_{s,z} \) of silicene decreases fast with \( E_z \) (Fig. 2(a)). To better understand \( \tau_{s,z} \) dependence on \( E_z \), we compare FPDM \( \tau_{s,z} \) with
the model calculations based on EY ($\tau_{s,z}^{EY}$), DP ($\tau_{s,z}^{DP}$) and EY+DP ($\tau_{s,z}^{E+DP}$) mechanisms as introduced earlier, in Fig. 2(b) and 2(d). From Fig. 2(b) for silicene, we show that $\tau_{s,z}^{E+D}$ and $\tau_{s,z}^{DP}$ approximately agree with FPDM $\tau_{s,z}^{a}$ in trends. For germanene, however, from Fig. 2(d) we find that $\tau_{s,z}^{EY}$ is in good agreement with the FPDM $\tau_{s,z}^{a}$, but neither $\tau_{s,z}^{E+D}$ nor $\tau_{s,z}^{DP}$ capture the qualitative trend. Therefore, $z$-direction spin relaxation in germanene should be mostly driven by EY mechanism, insensitive to $E_z$. The suppression of DP mechanism in germanene under finite $E_z$ may be due to the huge $B^{in}$ anisotropy $B^{in}_{z}/B^{in}_{x}$ (see Fig. 1(d) and Fig. S6(b)): as $B^{in}_{z}$ is so strong, any in-plane spins will be quickly relaxed and all spins are pinned along $z$; thus the total spin can only decay through direct spin-flip processes but not through spin precession driven by $B^{in}$ which changes spin direction gradually.

**Temperature dependence of $\tau_{s,z}$ and spin-valley locking.** It is important to understand the sensitivity of spin lifetime to temperature and determine the optimal operating temperature. Therefore, we show temperature dependence of $\tau_{s,z}$ without $E_z$ and with $E_z = 2$ and 5 V/nm (higher than $E_{cr}$ by $\sim$ 2 V/nm) in intrinsic silicene and germanene respectively in Fig. 3(a) and (b). Without $E_z$, $\tau_{s,z}$ of both silicene and germanene increase fast on cooling. This is the usual behavior of EY spin lifetime simply due to weaker e-ph scattering with lowering temperature. Since phonon occupation is smaller at a lower temperature, $\tau_p$ is longer (Fig. S8), so $\tau_s$ is longer ($\tau_s \propto \tau_p$ with EY mechanism). Under finite $E_z$, $\tau_{s,z}$ of germanene are similar to the values under zero $E_z$ as shown in Fig. 2(b), which are expected from the discussions on $E_z$ dependence of germanene above. In sharp contrast, finite $E_z$ significantly reduces $\tau_{s,z}$ of silicene and modifies the temperature dependence. To interpret such complex temperature dependence, in Fig. 3(c), we compare FPDM $\tau_{s,z}$ and the model ones $\tau_{s,z}^{EY}$, $\tau_{s,z}^{DP}$ and $\tau_{s,z}^{E+D}$ for silicene. All model relations fail to reproduce the temperature dependence under finite $E_z$ for silicene. The failure of the DP relation in particular below 200 K is probably because it is inapplicable for weak scattering regime (weak e-ph scattering at low temperatures). Other relations have been proposed for weak scattering e.g., $\tau_s \sim |\Omega|^{-1}$ and $\tau_s \sim 2\tau_p$, but none can capture the correct temperature dependence of $\tau_{s,z}$ of silicene under finite $E_z$, e.g., $\tau_s \sim |\Omega|^{-1}$ predicts $\tau_{s,z} < 20$ ps at all temperatures investigated here. Our theoretical studies highlight the importance of simulating spin lifetime using FPDM method for reliable prediction of spin lifetimes for large variations of external conditions.

Since the bands near the Fermi energy are composed of the Dirac cone electrons around $K$ and $K'$ valleys in silicene and germanene, spin relaxation process mostly arises from in-
tervalley and intravalley scatterings. To scrutinize contributions of intervalley and intravalley scatterings to spin lifetime, we examine relative intervalley spin relaxation contribution $\eta$ of germanene as a function of excess carrier density $n$, which is electron density $n_e$ minus hole density $n_h$, and controlled by chemical potential $\mu$. Positive carrier density corresponds to electron doping. 

(a) $\tau_{s,z}$ and (b) relative intervalley spin relaxation contribution $\eta$ of germanene as a function of excess carrier density $n$, which is electron density $n_e$ minus hole density $n_h$, and controlled by chemical potential $\mu$. Positive carrier density corresponds to electron doping. 

(c) $\tau_{s,z}$ of germanene as a function of in-plane magnetic field $-B_x$. 

(d) $\tau_{s,z}$ of germanene as a function of impurity density $n_i$ of neutral Ge vacancy (with $n_e$ and $n_h$ kept the same as intrinsic germanene). 

Formally the terminology “spin-valley locking” means that spin index (spin-up and spin-down) becomes locked with the valley index (e.g., $K$ and $K'$). This implies that (i) two valleys (e.g., $K$ and $K'$) exist with opposite spin polarizations. (ii) Within one valley, spins are all highly polarized along one direction, and carriers should have the same sign of spin. This needs large SOC splitting, i.e., the spin-up and down bands being largely separated.

Point (ii) will cause highly suppressed intravalley spin relaxation (i.e., relaxation through scattering processes within one valley). We explain the reason using germanene as an example: Under 5 V/nm, the SOC splitting for germanene is large, 23 meV at $K$. To have spins with the same sign, most of carriers should be located around the band edges (which require low temperatures and low carrier densities). Then the intravalley spin-flip transition between an occupied state at band edges and an empty state at the second conduction/valence band will be rather weak at relatively low temperatures, since phonon occupation becomes negligible at the corresponding phonon energy (comparable to SOC splitting).
for germanene, see Fig. S7). Therefore, with spin-valley locking, spin relaxation through e-ph scattering (mostly intervalley) will be highly suppressed leading to long spin lifetime, because of small phonon occupations at relatively low temperatures.

The existence of spin-valley locking not only leads to long spin lifetime but also allows the utilization of previously developed valleytronic technologies to design germanene-based devices. Our calculations provide guidance on the necessary conditions to realize spin-valley locking in germanene.

Carrier density and magnetic field dependence of \( \tau_{s,z} \) for Germanene at low T. As intervalley scattering was shown being dominant in germanene at 50 K with a very long spin lifetime, we further investigate its spin relaxation as a function of carrier density, which can be easily tuned by electrical gate experimentally. We will also determine the range of carrier density where spin-valley locking happens.

As shown in Fig. 4(a), we plot \( \tau_{s,z} \) of germanene as a function of excess carrier density \( n \) (which is electron density \( n_e \) minus hole density \( n_h \), and controlled by chemical potential \( \mu \)). We found it is very sensitive to \( n \) at the degenerate doping range (\( n \gtrsim 4 \times 10^{10} \text{ cm}^{-2} \), corresponding to \( \mu \) above the conduction band minimum). As the carriers contributing to spin relaxation have higher energies when \( n \) increases, the strong \( n \) dependence of \( \tau_{s,z} \) should be mainly a result of the strength of the e-ph scattering being enhanced at higher energies (Fig. S10).

Moreover, we find that the relative inter-valley spin relaxation contribution \( \eta > 0.9 \) at \( n \lesssim 4 \times 10^{10} \text{ cm}^{-2} \) under \( E_z = 5 \text{ V/nm} \) in Fig. 4(b). This indicates spin relaxation being dominated by inter-valley processes and the presence of spin-valley locking at the corresponding condition, consistent with our above discussions about spin-valley locking.

We then investigate effects of spin-valley locking under in-plane magnetic-field \( B_x \). From Fig. 4(c) at 50K for germanene, \( B_x \) has weak effects on spin lifetime of germanene under finite \( E_z \). This is because the applied external magnetic field is too weak compared with internal B field \( B^{in} \) under finite \( E_z \). This weak \( B_x \) dependence of spin lifetime is often used as an experimental evidence of spin-valley locking.

### Impurity effects and spin diffusion length.

Finally, we investigate the effects of the electron-impurity scattering. As an initial theoretical investigation, we will consider only one common neutral defect in germanene in this work - single Ge atom vacancy. From Fig. 4(d), we observe that \( \tau_{s,z} \) are reduced by introducing impurities and the reduction becomes significant when impurity density \( n_i \) approaches \( 10^{12} \text{ cm}^{-2} \). Another interesting observation is that under finite \( E_z = 5 \text{ V/nm} \), \( \tau_{s,z} \) reduces much less than the one with \( E_z = 0 \). Our simulations suggest that if \( n_i \) can be controlled below \( 10^{12} \text{ cm}^{-2} \), especially under a finite \( E_z \), germanene can exhibit long spin lifetime over 100 ns at or below 50 K.

At the end, we compute in-plane spin diffusion length \( l_{||,s} \) for \( z \)-direction (out-of-plane) spin polarization of germanene using the relation \( l_{||,s,z} = \sqrt{D \tau_{s,z}} \), where \( D \) is diffusion coefficient. \( D \) can be estimated using the general form of Einstein relation \[ D = \mu e / (d(n_e+n_h) / d\mu) \], where \( \mu e \) is the average of electron and hole mobility, which are obtained from solving Boltzmann equation as detailed in the method section. From Table 1, we can see \( l_{||,s} \) of germanene at 300 K is 2-3 \( \mu \)m, shorter than the longest measured value of graphene samples, \( \sim 12 \mu \)m. At 50 K, as mobilities are higher and \( \tau_{s,z} \) are longer, \( l_{||,s} \) become 400 \( \mu \)m without impurities and 120 \( \mu \)m with \( n_i = 10^{11} \text{ cm}^{-2} \), which are much longer than experimental values of graphene at different temperatures ranging from 1 to 40 \( \mu \)m.

### Conclusions

By employing our newly developed first-principles density-matrix dynamics approach, we computed spin lifetime of two Dirac 2D materials - silicene and germanene as a function of temperature, electrical doping and neutral impurities, as well as applied electric and mag-
We find silicene and germanene have qualitative different spin relaxation mechanisms under finite $E_z$ fields. We did systematic comparisons between our FPDM $\tau_s$ and those estimated by phenomenological models with first-principles input parameters. We find that germanene out-of-plane spin relaxation can be qualitatively understood by EY relation, regardless of the one with and without E field. On the other hand, spin relaxation in silicene is more complicated: although at room temperature, the trends of $E_z$ dependence of silicene $\tau_{s,z}$ can be captured by a combination of EY and DP relation, the temperature dependence of $\tau_{s,z}$ under finite $E_z$ cannot be explained by any simplified model relations.

We demonstrated giant spin lifetime anisotropy (two order of magnitude higher than graphene) and provided the condition for spin-valley locking with long spin lifetime in germanene. Specifically, we show that at a low T - 50 K, $\tau_s$ of germanene can reach 100 ns and $l_s$ can exceed 100 $\mu$m (longer than graphene samples), if impurity density is controlled low ($\leq 10^{11}$ cm$^{-2}$). This is very promising because the spin-valley locking property has only been realized in either TMDs which usually have much lower carrier mobility, or graphene on substrates which have complexity of interfacial engineering. The realization of spin-valley locking in single materials with long spin lifetime and ultrahigh mobility opens up highly promising pathways for spin-valleytronics applications.

### Methods

To predict spin relaxation time from first principles, we employ our newly developed ab initio density-matrix dynamics approach, which includes quantum descriptions of various scattering processes and is applicable to general solid-state systems. The density matrix master equation due to the e-ph and e-i scattering in interaction picture reads:

$$\frac{d\rho_{12}(t)}{dt} = \frac{1}{2} \sum_{345} \left\{ \left[ I - \rho(t) \right]_{13} \rho_{45}(t) \times \left[ P_{32,45}^{e-ph}(t) + P_{32,45}^{e-i}(t) \right] \ight.$$  
$$- \left[ I - \rho(t) \right]_{45} \rho_{32}(t) \times \left[ P_{45,13}^{e-ph}(t) + P_{45,13}^{e-i}(t) \right] ^* \right\} + H.C.,$$  

where $\rho$ is density matrix. H.C. is Hermitian conjugate. The subindex, e.g., “1” is the combined index of k-point and band. The weights of k points must be considered when doing sum over k points. $P_{e-ph}^c$ and $P_{e-i}^c$ are the generalized scattering-rate matrices for the e-ph and e-i scattering respectively. Note that $P^c$ with $c$ being a scattering channel is related to its value $P^{s,c}$ in the Schrodinger picture as $P_{1234}^c(t) = P_{1234}^{s,c} \exp [i (\varepsilon_1 - \varepsilon_2 - \varepsilon_3 + \varepsilon_4) t]$. $P^{s,c}$ is time independent and is computed from

| T (K) | $n_i$ (cm$^{-2}$) | $\overline{\mu}$ (cm$^2$/V/s) | $D$ (cm$^2$/s) | $\tau_{s,z}$ (ns) | $l_{s,z}$ ($\mu$m) |
|------|------------------|-------------------------------|---------------|------------------|-----------------|
| 300  | 0                | $3.2 \times 10^4$             | 830           | 0.1              | 2.9             |
| 300  | $10^{11}$        | $2.5 \times 10^4$             | 620           | 0.1              | 2.5             |
| 50   | 0                | $3.8 \times 10^6$             | 16700         | 97               | 400             |
| 50   | $10^{11}$        | $4.5 \times 10^5$             | 2000          | 76               | 120             |
| 50   | $10^{12}$        | $5.8 \times 10^4$             | 250           | 26               | 25              |

Table 1: Spin dynamic and transport properties of intrinsic germanene under $E_z=5$ V/nm without and with neutral impurities (with impurity density $n_i$). $\overline{\mu}$ is the average of electron and hole mobility. The method of calculating mobility is given in Supporting Information. The theoretical results of electron and hole mobility are given in Fig. S8. $D$ is diffusion coefficient. $l_{s,z}$ is spin diffusion length of $z$-direction spin. The formula computing $D$ and $l_{s,z}$ are given in the main text.
corresponding e-ph or e-i matrix elements and electron and phonon energies.

All energies and matrix elements are calculated on coarse $k$ and $q$ meshes using the DFT software JDFTx\textsuperscript{44} and are then interpolated to extremely fine meshes in a basis of maximally localized Wannier functions.\textsuperscript{45–47} Starting from an initial state with a net spin, we evolve the density matrix $\rho(t)$ through the master equation Eq. 1 for a long enough simulation time, typically from ns to $\mu$s. We then obtain the evolution of spin observable $S_i(t)$ ($i = x, y, z$) from $\rho(t)$ (Eq. S1). At the end, spin lifetime $\tau_{s,i}$ is obtained by fitting $S_i(t)$ to an exponential decay curve with decay constant $\tau_{s,i}$.

More details are given in Supporting Information Sec. SI and SII and Ref. 29.

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\textsuperscript{12} (Supporting Information Sec. SVI).

### Author contributions

J.X. and H.T. performed the ab initio calculations and analyses. R.S. and Y.P. designed and supervised all aspects of the study. All authors contribute to the writing of the manuscript.

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