Breakdown of the Hebel-Slichter effect in superconducting graphene due to the emergence of Yu-Shiba-Rusinov states at magnetic resonant scatterers

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(Dated: February 15, 2019)

We study theoretically the relaxation of electron spins in graphene in proximity to an s-wave superconductor in the presence of resonant magnetic and spin-orbit impurities. Off resonance, the relaxation behaves as predicted from superconducting coherence: with lower temperatures the spin relaxation increases when electrons scatter off magnetic impurities (Hebel-Slichter effect), and decreases when the scatterers induce spin-orbit coupling. This distinct temperature dependence, not available in the normal state, can uniquely discriminate between the two scattering mechanisms. But the Hebel-Slichter picture breaks down at resonances. The emergence of Yu-Shiba-Rusinov bound states within the superconducting gap shifts the spectral weight of the magnetic resonances and leads to a significant decrease of the spin relaxation rate at lower temperatures. Our findings should be valid for generic s-wave superconductors that host resonant magnetic impurities.

PACS numbers: 72.80.Vp, 72.25.Rb

Keywords: superconductivity, graphene, spin relaxation, resonance, Yu-Shiba-Rusinov states, Hebel-Slichter effect

Introduction: Superconducting spintronics strives at combining both spintronics [1] and superconductivity (SC) [2–4] to find new phenomena. While the latter can be used as an efficient dissipationless source, the former exploits spin for logical operations. Therefore one can hope to launch a superconducting (SC) spin-operating device that would be, on the one hand, very efficient in terms of energy demands, but on the other hand, would offer complex logical performance and fine-tuned functionality. A potentially versatile platform for that is offered by layered, high-mobility 2D materials that are susceptible to superconductivity, while the reduced spatial dimensionality supports topological protection, non-Abelian statistics, and switchable bulk/edge transport. Recent experimental demonstration of SC in the twisted bilayer graphene [5], 2D topological insulators [6, 7], and layerd transition-metal dichalcogenides [8–12] drive considerable theoretical, and technological interests in that regard.

A limiting factor for spin-based logical performance is spin relaxation (SR) [13–22]. In this Letter we explore spin relaxation in SC-graphene focusing on magnetic resonant impurities, and impurities locally enhancing spin-orbit-coupling (SOC). Both are, per se, at the heart of intensive scientific discussions [23–29] about the dominant SR mechanism in graphene. We demonstrate that the s-wave SC in graphene can offer an ultimate answer capable to discriminate between them. This is because unlike in the normal phase, the proximity induced SC gap, strong temperature-dependence in carriers population, underlying coherence phenomena, and the potential appearance of bound states, heavily influence spin-flip dynamics in the SC phase. We believe that despite its experimental challenge, our predictions have a potential to drive the forthcoming spintronics activities into the realm of superconducting graphene (SCG).

Theoretical studies of SCG started more than a decade ago [30–34]. Soon, it became clear that weak electron-phonon coupling, and low electronic densities (at experimentally accessible dopings) are not sufficient to cause the Cooper instability [32–34]. One possibility to overcome that would be a proximity to superconductor [35–37], or alkaline intercalation [38, 39] that enhances electronic density and also coupling with phonons. Theoretical models at elevated Fermi energies (µ > 1 eV), and especially at regions near the van Hove singularities (µ > 2.7 eV), offer a plethora of ‘possible exotic SC pairing mechanisms’, that count: p-wave, extended s-wave, (singlet) chiral d-wave, (triplet) f-wave, and also their simultaneous co-existences; for details see [40–47]. The first experimental demonstration of SCG [48] dates to 2007, where metallic contacts in a lateral Josephson geometry induced SC in graphene by the proximity effect [49–51]. The higher degree of functionality brings the interfacial geometry, where graphene grows directly on top of a superconductor [52–55]. At the same time, the predicted SC phase in alkaline intercalated graphite structures were successfully verified [51–55]. The reported experimental findings vary by method, but the typical magnitudes of the induced SC gap ranges from few tens of µeV [48] up to 1 meV [57] (∼ 7 K). Also, both s-wave [48] and p-wave [53] SC pairings were convincingly demonstrated; for more details see the comprehensive review [58].

Rationale: SR of quasi-paricles (QP) in the SC phase depends on the underlying scattering mechanism, namely, its time-reversal parity. The latter determines how the electron and hole transition amplitudes combine before squaring that gives the final spin-flip rate. As pointed out by Yafet [59], the SR-rate in SC phase, 1/τ_{SC}, relates—within the first-order perturbation theory—to its normal phase counterpart, 1/τ_{N}(E).
Graphene chemical potential $\mu$ for 100 ppm of resonant impurities. A pronounced resonant peak emerges at $\mu = 24$ meV; the background gray line displays DOS of the unperturbed system. Black, red, green, and blue vertical lines represent particular resonant, and off-resonant chemical potentials at which we turn the system into SC phase with a SC-gap $\Delta_0 = 5$ meV. The corresponding QP-DOSs at those chemical potentials are shown at (b). Black x-symbols stand for $\mu = 24$ meV, red triangles for $\mu = 45$ meV, green squares for $\mu = 90$ meV, and blue circles for $\mu = 180$ meV. Dashed lines with the same color serve as guides for eyes and display QP-DOSs in the unperturbed SCG. QP resonant enhancement near the coherence peaks appear for chemical potentials close to the resonances in the normal phase. Inset: adatom absorbed on SCG with its pictorial tight-binding description. For all plots we used hybridization $\omega = 5.5$ eV, and on-site energy $\varepsilon = 0.26$ eV.

### Model and Methodology

To describe the singlet SC in graphene in the proximity to a superconductor we use the established tight-binding model \[30\]:

$$H_0 = -\sum_{m\sigma} \left(t\delta_{(mm)} + \mu\delta_{mn}\right)c^\dagger_m\sigma c_n\sigma + \Delta \sum_m c^\dagger_m c^\dagger_{m+1} + hc.$$  

(1)

Here $t = 2.6$ eV stands for the conventional NN hopping, $\mu$ for the underlying chemical potential (doping level) with reference at the Dirac point of the normal phase, and $\Delta$ for $T$-dependent global on-site s-wave-pairing. We assume BCS dependence of the graphene SC-gap on $T$, $\Delta = \Delta_0 \text{tanh}[1.74 \sqrt{T_c/T} - 1]$, with proximity relevant value of $\Delta_0 = 1$ meV and $T_c \approx 7$ K. Operator $c^\dagger_{m\sigma}$ annihilates (creates) an electron with spin $\sigma$ at a graphene lattice site $m$, $\delta_{mn}$ represents the usual Kronecker-symbol, and $\delta_{(mn)}$ its NN analog—that is unity for the direct nearest-neighbors, and zero otherwise. The orbital interaction with an adatom—annihilation and creation operators $d^\dagger_\sigma$ and $d^\dagger_\sigma$—is governed by the hybridization $\omega$, on-site energy $\varepsilon$ and proximity pairing $\Delta$ on the impurity site \[38\]:

$$V_o = \sum_{\sigma} \left((\varepsilon - \mu)d^\dagger_\sigma d_\sigma + \omega d^\dagger_\sigma c^\dagger_{0\sigma} + \Delta d^\dagger_\sigma d^\dagger_{1\sigma} + hc\right).$$  

(2)

For a pictorial definition of $V_o$ see the inset in Fig. [1]. The above orbital perturbation is completed by a local spin-dependent term $V_s$. Our analysis covers two ex-
FIG. 2. QP SR-rates in SCG at different temperatures (symbols) for 1 ppm of hydrogen (a), and fluorine (b) magnetic impurities as functions of $\mu$. Outside of the resonances SR-rates in SC-phases increase, in accordance with the Yafet prediction, contrary, in the resonances they decrease. Rainbow arrows indicate increasing or decreasing trends of SR-rates with lowered $T$ compared to the normal phase. The insets show the corresponding Hebel-Slichter ratios—$\left(1/\tau_{SC}\right)/\left(1/\tau_{N}\right)$ as functions of $T/T_c$—at two representative Fermi energies (indicated by black and red arrow ticks on the horizontal axis): resonant $-\mu = -80$ meV for hydrogen, and $-\mu = -300$ meV for fluorine—black circled data (values at left logarithmic axis!), and off-resonant $-\mu = 500$ meV for both cases—red circled data (values at right linear axis). Panels (c) and (d) show DOS in the normal phase in the presence of magnetic moments, and resonant (shaded) and off-resonant (white) doping regions; for the sake of visibility the impurity concentrations were exaggerated. Panels (e) and (f) display the energies of the subgap Yu-Shiba-Rusinov states for hydrogen and fluorine as functions of $\mu$. Smaller SR-rates in (a) and (b) are correlated with the resonances in the normal phase in (c) and (d), and the bound states in (e) and (f) with energies deep inside the SC-gap.

FIG. 3. QP SR-rates in SCG at different temperatures (different symbols) due to locally enhanced SOC for 1 ppm of hydrogen (a), and fluorine (b) impurities as functions of $\mu$. SR-rates decrease almost uniformly with the lowered $T$, their decrease becomes steeper and would saturate as $T \to 0$. Similarly as in the normal phase, at resonances SR-rates are enhanced. Rainbow arrows indicate decreasing trend of SR-rates with lowered $T$ compared to the normal phase.
perimentally important cases: (1) exchange interaction, \( V^{(1)} = -J \mathbf{S} \cdot \mathbf{s} \), between an itinerant spin \( \mathbf{s} \) at adatom-level [69] and a non-itinerant \( \frac{1}{2} \) impurity spin \( \mathbf{S} \) (e.g., inner shell, or Hubbard-like induced), and (2) local SOC in the vicinity of an adatom [70] [72] with enhanced Rashba and PIA strengths. For the explicit form of \( V^{(2)} \), see [73]. To work with realistic impurities we consider hydrogen and fluorine adatoms as both give sizable SOC enhancement [70] [71], and can also carry magnetic moments [70] [83].

Our methodology is standard: from \( H_0 \) at given \( \mu \) we compute: 1) eigenspectrum \( E_k = \sqrt{(\epsilon_k - \mu)^2 + \Delta^2} \), where \( \epsilon_k \) are known eigenvalues in the normal phase, 2) 'in' and 'out' scattering states \( |k, \sigma \rangle \)—QP Bloch levels normalized to unity, and 3) unperturbed (retarded) Green's function elements (normal and anomalous), \( G_0 \). From \( G_0 \) and \( V = V_c + V_A \) we get T-matrix, \( T = V \cdot (1 - G_0 \cdot V)^{-1} \), which gives rise to the scattering amplitudes, \( \langle k, \uparrow | T | q, \downarrow \rangle \), and perturbed Green's function \( G = G_0 + G_0 \cdot T \cdot G_0 \). We assume dilute concentration of impurities not affecting \( \Delta \), what liberate us from self-consistent calculations. Knowing \( G \) we compute (L)DOS, bound states, and other spectral features of the perturbed system, while from the scattering amplitudes we obtain spin-flip scattering rates. Finally, to get SR, \( 1/\tau_s \), at given \( \mu \) and \( T \) for a concentration \( \eta \) (per carbon atom) of spin-active impurities we evaluate the following integral over the 1st Brillouin zone:

\[
\frac{1}{\tau_s} = \int_{BZ} \int dq \ |\langle k, \uparrow | T | q, \downarrow \rangle|^2 \delta(E_k - E_q) \left( \frac{\partial \mu}{\partial E_k} \right)
\]

where \( g = 1/(\exp[\frac{E_q}{kT}] + 1) \) is the Fermi-Dirac distribution, and \( A_{wc} \) is the area of the graphene unit cell. The Yafet formula is as a special case of Eq. 3. Approximating \( T \approx V \), and plugging the exact expression for the QP-wave functions in terms of the corresponding electronic states in the normal phase (Bogoliubov transformation) one gets \( \langle k, \uparrow | V | q, \downarrow \rangle = (u_k u_q \pm v_k v_q) \langle V_s \rangle_{kq} \), where the last term is the normal phase matrix element for the spin-flip part of \( V \). Integration over \( q \)'s gives SR-rate at energy \( E_k \), and integrations over \( k \)'s account for thermal smearing.

Results: Adatoms on graphene give rise to resonances [85] [86]. Particularly those near the Dirac point strongly modify transport properties [85] [86]. Figure 1 demonstrates how resonances in the normal phase affect the population of QP states in SCG.

Figure 2 shows various characteristics for spin-flip scattering off magnetic impurities in the normal and SC graphene, for two representative impurities: hydrogen—panels (a),(c),(e), and fluorine—panels (b),(d),(f). Particularly, Figs. (a) and (b) display QP SR-rates in SCG at \( \Delta_0 = 1 \) meV for different temperatures in the presence of 1 ppm of magnetic impurities. We are plotting values of Eq. 1 for \( H_s = H_0 + V_c + V^{(1)} \), varying chemical potential \( \mu \), and SC-gap \( \Delta \) with temperature \( T \). Hydrogen [69] with magnetic moment—\( \omega = 7.5 \) eV, \( \varepsilon = 0.16 \) eV and \( J = -0.4 \) eV—gives rise in the normal phase to a narrow resonant region near the Dirac point; see the corresponding magnetic DOS at Fig. 2(d) [69] [83] with concentration \( \eta = 1 \%) \). How those resonances reflect on QP SR-rates is seen from Figs. (a) and (b). There, the shaded regions show the SR-rate in the normal phase \( (T = T_c) \), then lowering \( T \) in the SC phase we see a quite intriguing behavior: for the off-resonant doping regions \( 1/\tau_s^{SC} > 1/\tau_s^{N} \), and for fluorine—panels (d),(f) of SR-rate in the SC phase by almost a factor of 4 (graphs with red symbols), but in the resonant regions—for hydrogen \( \mu = -80 \) meV, and for fluorine \( \mu = -300 \) meV—we see a strong decrease of SR-rates (graphs with black symbols) by almost three-orders of magnitude! This suggests a nice experimental tool—observing enhanced and strongly depleted SR-rate in the SC phase when varying \( \mu \) and lowering \( T \) will signify the presence of resonant magnetic impurities!

To explain this peculiar decrease of SR in the resonances which is at odds with its normal phase behavior [69] [83] we calculate in Figs. (c) and (f) the corresponding energies (T-matrix singularities) of the Yu-Shiba-Rusinov magnetic bound states [96] [98], that emerge in the SCG [99]. We see that at resonances they...
are deep in the SC-gap. This offers an explanation why SR-rates dropped down. The resonant spin-flip scattering of QPs makes many contributions from multiple scatterings and virtual state tunnelings. Schematically, they can be written as $V_{aa} + V_{at} \frac{\langle I \rangle \langle I \rangle}{E_{a}-E_{t}+\mu_{a}} V_{t} + \cdots$, where $E_{t}$ represents energy of any intermediate state—extended, or the subgap one—and $E_{a}$ stands for the energy of an incident extended QP state. The dominant spin-flip matrix elements, $V_{at}$, are those for which the extended state $a$ overlaps with the magnetic impurity level $I=\text{YSR}$, since only this gives rise to QP spin flip. While $V_{at}=\text{YSR}$’s are roughly the same for $a$-states at the coherence peaks, what matters are the energy differences $E_{a} - E_{t}=\text{YSR}$ in the denominator. Those are small in the off-resonant region, since $E_{t}=\text{YSR}$ are aligned with the edges of the SC-gap, and are large in the resonances. That this would be the case of the reduced SR is also clear from the $T$-dependence of the SR-rates; for higher $T$ the SC-gap $\Delta$ gets smaller, and hence also the difference $E_{a} - E_{t}=\text{YSR}$. It is worth to stress that from the original Yafet formula one would get exactly the opposite conclusion. It is because the formation of the bound states in the SC-gap, and their role in the virtual scattering processes were not taken into account. At sub-Kelvin temperatures—data for $T = 100 \text{mK}$ displayed by dashed lines in Figs. 2(a) and (b)—the SR-rates at low dopings drop down. This is because the QP DOS($E$) = $\frac{E}{\sqrt{E^{2}-\Delta^{2}}} \text{DOS}(\mu)(-\frac{\partial g}{\partial E})$, becomes substantially suppressed by the thermal Fermi-Dirac smearing. At larger dopings this is countered by higher DOS($\mu$).

Figure 3 shows SR-rates at different temperatures as functions of chemical potential for the Elliott-Yafet [100, 101]. SR mechanism—scattering off hydrogen (a) and fluorine (b) impurities in the presence of strong local SOC, $V_{t}^{(2)}$, which incorporates realistic, first-principles motivated coupling strengths, see [73]. As predicted by Yafet [59] and quantitatively computed by our full T-matrix calculation, SR-rates for both considered cases decrease with the lowered $T$ by an order of magnitude over the whole range of chemical dopings giving rise to a sizeable signal. Despite that uniform decrease, in the resonances SR-rates get enhanced as was the case also in the normal phase [102]. This is because a QP locked in the resonance has enough time to experience SOC, that despite enfeebled in the SC phase, can flip its spin. As an experimental protocol—a global decrease of the SR-rate with lowered $T$ over whole ranges of $\mu$ would signal a SOC-dominated relaxation.

Conclusions: We discussed SR in graphene in the proximity of $s$-wave superconductor in the presence of resonant impurities. We demonstrated that compared to the normal phase, the spin-flip dynamics in the SC phase allows to discriminate between the magnetic moment-dominated SR, and SOC-dominated one. Our theory predicts that reaching superconducting resonances the former would significantly decrease—alike the anti-Hebel-Slichter effect—due to the deep-lying subgap Yu-Shiba-Rusinov states. The predicted effect can reach three-to-four orders of magnitude making it robust, and verifiable by experiment.

Acknowledgements: D.K. thanks Drs. Ferenc Simon, Lucía Komendová, and Benedikt Scharf for useful discussions, and Dr. Jeongsu Lee for helpful tips regarding numerical implementation. Authors acknowledge supports from DFG SFB 1277, and the EU Seventh Framework Programme under Grant Agreement No. 604391 Graphene Flagship.
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SUPPLEMENTAL MATERIAL

In the Letter we use the local adatom-induced SOC Hamiltonian, $V_{s}^{(2)}$, that is based on local symmetries \[74\] and whose couplings are fitted to first-principles calculations; for details concerning Hydrogen, see \[70\], and for Fluorine \[71\]. Since the weak SOC of the pristine graphene does not play a significant role we focus on the locally induced SOC effects in the vicinity of adatoms. The defect region consists of the adatomized carbon ($m = 0$), and sets C$_{nn}$ and C$_{nnn}$ of its three nearest (nn) and six next-nearest (nnn) neighbors. A realistic effective SOC Hamiltonian based on local symmetries reads:

$$V_{s}^{(2)} = \frac{i\Lambda^{A}}{3\sqrt{3}} \sum_{m \in C_{nnn}} \sum_{\sigma} c_{0\sigma}^\dagger \left( \hat{s}_{z} \right)_{\sigma\sigma} c_{m\sigma} + h.c.$$ 

$$+ \frac{i\Lambda^{B}}{3\sqrt{3}} \sum_{m,n \in C_{nn}} \sum_{\sigma, \bar{\sigma}} c_{m\sigma}^\dagger \nu_{mn} \left( \hat{s}_{z} \right)_{\sigma\sigma} c_{n\bar{\sigma}} + h.c.$$ 

$$+ \frac{2i\Lambda^{R}}{3} \sum_{m \in C_{nn}} \sum_{\sigma \neq \bar{\sigma}} c_{0\sigma}^\dagger \left( \hat{s} \times d_{0m} \right)_{z,\sigma\sigma'} c_{m\sigma'} + h.c.$$ 

$$+ \frac{2i\Lambda^{PIA}}{3} \sum_{m,n \in C_{nn}} \sum_{\sigma \neq \bar{\sigma}'} c_{m\sigma}^\dagger \left( d_{mn} \times \hat{s} \right)_{z,\sigma\sigma'} c_{n\bar{\sigma}'} + h.c.$$ 

Symbol $\hat{s}$ represents an array of the Pauli matrices acting in spin space. The sign factor $\nu_{mn}$ equals $-1$ ($+1$) if the next-nearest hopping $n \rightarrow l \rightarrow m$ via a common neighbor $l$ becomes (counter)clockwise and a unit vector $d_{mn}$ points from site $n$ to $m$. The first two terms in Eq. (4) are the local intrinsic SOCs associated with sublattices A and B, respectively, the third is the local Rashba SOC, and the last two terms are the local pseudospin inversion asymmetry (PIA) induced SOC for sublattices A and B, respectively; for more details see \[74\]. The graphical representation of local SOC hoppings is depicted in Fig. 4. The numerical values of these parameters for hydrogenated and fluorinated graphene are summarized in Table I. We adopted those values in our numerical calculations of the spin relaxation in SC phase.

| Adatom    | $\Lambda^{A}$ | $\Lambda^{B}$ | $\Lambda^{R}$ | $\Lambda^{PIA}$ | $\Lambda^{PIA}$ |
|-----------|---------------|---------------|--------------|-----------------|-----------------|
| Hydrogen  | -0.21         | 0             | 0.33         | 0               | 0.77            |
| Fluorine  | 0             | 3.3           | 11.2         | 0               | 7.3             |

Table I. Spin-orbital tight-binding parameters (in meV) entering the model Hamiltonian $V_{s}^{(2)}$. 

FIG. 4. Schematic representation of the local SOC strengths in the vicinity of adatom that enter SOC Hamiltonian $V_{s}^{(2)}$. Blue and red arrows label spin-flipping and spin-conserving SOC hoppings, respectively, which connects specific nearest, or next-nearest neighbor carbons.