Spin relaxation mechanism in graphene: resonant scattering by magnetic impurities

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It is proposed that the observed small (100 ps) spin relaxation time in graphene is due to resonant scattering by local magnetic moments. At resonances, magnetic moments behave as spin hot spots: the spin-flip scattering rates are as large as the spin-conserving ones, as long as the exchange interaction is greater than the resonance width. Smearing of the resonance peaks by the presence of electron-hole puddles gives quantitative agreement with experiment, for about 1 ppm of local moments. While the local moments can come from a variety of sources, we specifically focus on hydrogen adatoms. We perform first-principles supercell calculations and introduce an effective Hamiltonian to obtain realistic input parameters for our mechanism.

Graphene [1,2] has been considered an ideal spintronics [3,4] material. Its spin-orbit coupling being weak, the spin lifetimes of Dirac electrons are expected to be long, on the order of microseconds [3]. Yet experiments find tenths of a nanosecond [5,6]. This vast discrepancy has been the most outstanding puzzle of graphene spintronics. Despite intense theoretical efforts [11,21], the mechanism for the spin relaxation in graphene has remained elusive. Recently, mesoscopic transport experiments [22] found evidence that local magnetic moments could be the culprits. Here we propose a mechanism of how even a small concentration of such moments can drastically reduce the spin lifetime of Dirac electrons. If the local moments sit at resonant scatterers, such as vacancies [23,25] and adatoms [25,26], they can act as spin hot spots [27]: while contributing little to momentum relaxation, they can dominate spin relaxation. Although our mechanism is general, we specifically assume that local moments come from hydrogen adatoms. The calculated spin relaxation rates for 1 ppm of local moments, when averaged over electron density fluctuations due to electron-hole puddles, are in quantitative agreement with experiment. Our theory shows that in order to increase the spin lifetime in graphene, local magnetic moments at resonant scatterers need to be chemically isolated or otherwise eliminated.

Magnetic impurities typically do not play a role in the electron spin relaxation of conductors [3], unless when doped with transition metal elements. In graphene the presence of local magnetic moments is not obvious, unless the magnetic sites (vacancies or adatoms) are intentionally produced [21,25]. It is reasonable to expect that there are not more magnetic sites than, say, 1 ppm, in graphene samples investigated for spin relaxation. For this concentration a simple estimate gives a weak spin relaxation rate, similar to what is predicted for spin-orbit coupling mechanisms. Indeed, the Fermi golden rule gives, for exchange coupling \( J \) between electrons and local moments, spin relaxation rate \( \frac{1}{\tau_s} \approx \frac{2\pi}{\eta} J^2 \nu_0(E_F) \), where \( \nu_0(E_F) \) is graphene’s density of states at the Fermi level and \( \eta \) is the concentration of the moments. Taking representative values of \( J \approx 0.4 \) eV, \( \eta \approx 10^{-6} \), and \( E_F \approx 0.1 \) eV (for which \( \nu_0 \) is about 0.01 states per eV and atom), one gets spin relaxation times of 100 ns, three orders below the experimental 100 ps.

What we show in this paper is that the spin relaxation due to magnetic impurities in graphene is significantly enhanced by resonant scattering, for which the perturbative Fermi golden rule does not apply. The intuitive idea is that if the exchange coupling \( J \) is greater than the resonance width \( \Gamma \), the electron spin can precess at resonance by at least one period during the interaction time with the impurity. Then the spin-flip probability becomes as likely as the spin-conserving one. This idea is confirmed by an explicit calculation for graphene with a hydrogen adatom. We use a supercell first-principles band structure to investigate the local magnetic moments (as has been done earlier [26]) and parameterize the band structure in terms of effective exchange couplings, to obtain their realistic estimates. We then use a single impurity spin model with exchange on the resonance site to calculate the T-matrix and spin relaxation rate. Finally, we illustrate the intuitive picture of resonant spin enhancement on a toy one-dimensional model of an electron scattering off a magnetic moment in a resonant quantum well.

Spin-polarized band structure of hydrogenated graphene. The electronic structure of a relaxed \( 5 \times 5 \) supercell with a single H atom on top of a C atom (denoted below as \( CH \)) has been calculated within density functional theory using the full-potential linearized augmented plane wave method as implemented in the FLEUR code [28]. Figure 1(a-f) shows the results. The valence and conduction bands are separated at K point due to covalent bonding of carbon \( p_z \) and hydrogen \( s \) orbitals by about 1 eV. In between lies the mid-gap band formed mainly by \( p_z \) orbitals of C atoms closest to H. The ground state is ferromagnetic, with the exchange splitting of about 0.1 eV. The magnetic moment is significant in a close neighborhood of \( CH \).
H to H are captured by on-site energy terms, indicated in Fig. 1(g). The orbital effects due to H region. Here $J_{h}$ is on the nearest neighbors to C. The orbital effective from the Fermi level, whose character is less influenced maximal and gradually decreases for the bands away to the third nearest carbon atoms to C. Hence the spin splitting of the mid-gap states is exchange hopping model of Eq. (1). (a) Spin-polarized band structure. (b) Total density of states per atom (filled) and $p_{z}$ projected local densities summed up to the third nearest carbon atoms to C$_{H}$, normalized to the corresponding number of atoms in the set. Exchange splittings of the conduction (c), mid-gap (d), and valence (e) bands. Solid lines are from the model. (f) Local magnetic moments around hydrogen, indicated in $\mu_{B}$. (g) Exchange hopping model of Eq. (1).

The fits, shown in Fig. 1(a) and detailed in Fig. 1(c-e), are remarkably good especially around K. We find that $J_{h}$ alone controls the exchange splitting of the valence and conduction bands in a large region around K point.

**Resonant scattering by magnetic impurities.** To solve the magnetic scattering problem using $H'_{\text{eff}}$ in the single impurity limit is numerically demanding. However, the most important spin-flip contribution is expected to come from the exchange coupling on the resonant scatterer (H atom) site. We thus neglect $J_{1}$ and $J_{2}$ terms and propose the reduced Hamiltonian, $H'(\hat{S})$:

$$H'(\hat{S}) = \sum_{\sigma} \varepsilon_{\ell}(\sigma) c_{\ell,m_{\sigma}}^{\dagger} c_{\ell,m_{\sigma}} + T c_{\ell,m_{\sigma}}^{\dagger} c_{\ell+1,m_{\sigma}} - J \hat{S} \hat{S}.$$  

The exchange term describes the interaction of electron spin $\hat{S} = h_{\alpha} h_{\beta}$ and impurity moment $\hat{S}$. We keep orbital parameters $\varepsilon_{\ell} = 0.16 \text{ eV}$ and $T = 7.5 \text{ eV}$, and take a generic value $J = -0.4 \text{ eV}$ for exchange. The spin relaxation rates, when broadened by puddles, are hardly influenced by the precise value and the sign of $J$.

In the independent electron-impurity picture (we do not discuss Kondo physics), total Hamiltonian $H_{0} + H'(\hat{S})$ diagonalizes in the singlet ($\ell = 0$) and triplet ($\ell = 1$) basis ($\ell$, $m_{\ell}$) (here $m_{\ell}$ runs from $-\ell$ to $\ell$). Eliminating by downfolding (Löwdin transformation) H orbitals, we arrive at the single-site impurity Hamiltonian,

$$H'_{\text{fold}}(\hat{S}) = \sum_{\ell,m_{\ell}} \alpha_{\ell}(E) c_{\ell,m_{\ell}}^{\dagger} c_{\ell,m_{\ell}},$$  

where the energy-dependent on-site coupling is,

$$\alpha_{\ell}(E) = \frac{T^{2}}{E - \varepsilon_{\ell} + (4\ell - 3)J}.$$  

The orbital parameters $\varepsilon_{\ell} = 0.16 \text{ eV}$ and $T = 7.5 \text{ eV}$ were fitted already in Ref. [31]. Least-square fitting the model Hamiltonian $H'_{\text{eff}}$, Eq. (1), to our supercell spin-polarized first-principles data, gives $J_{h} = -0.82 \text{ eV}$, $J_{1} = 0.69 \text{ eV}$, and $J_{2} = -0.18 \text{ eV}$. We fitted the valence, mid-gap, and conduction bands at 100 equidistant points along GKMFG.
different for singlet and triplet states.

The T-matrix elements for the above impurity problem can be calculated as (see, e.g., [33])

$$T(E)_{\kappa',\ell',m'_{\ell'}}(\kappa,\ell,m_{\ell}) = \frac{1}{N_C} \frac{\delta_{\kappa,\kappa'} \delta_{m_{\ell},m'_{\ell'}}}{1 - \alpha_{\ell}(E) G_0(E)} \alpha_{\ell}(E) .$$

where $\kappa$ labels momentum and band index of graphene’s Bloch states, $N_C$ is the number of carbon sites in the sample, and $G_0(E)$ is the retarded Green function per carbon atom and spin of unperturbed graphene. Near the neutrality point ($E = 0$), $G_0(E) \approx \frac{D}{\pi} \left| \frac{\ln(\pi^2 - E^2)}{E} \right| - i \pi \text{sgn}(E) \Theta(D - |E|)$, where the graphene bandwidth $D = \sqrt{3\pi} \approx 6$ eV.

Resonant states appear for energies $|E| < D$ at which the real part of the denominator of Eq. (5) equals zero. Near the neutrality point ($|E| << D$) we get the equation

$$E_{\text{res},\ell} = \frac{T^2}{D^2} \ln \frac{E_{\text{res},\ell}^2}{D^2} = \varepsilon_h - (4\ell - 3)J$$

which determines the resonant energies $E_{\text{res},\ell}$ for singlet and triplet states. For a non-magnetic impurity ($J = 0$) there appears a single resonant level close to the neutrality point [30]. For a magnetic impurity this level splits to singlet and triplet peaks, and shifts in energy. For $J < 0$ the singlet resonance has a lower energy, see [32].

From the T-matrix we obtain spin-flip rate $1/\tau_s$ at zero temperature (thermal broadening is discussed in [32]).

$$1/\tau_s = \frac{2\pi}{\hbar} \frac{\text{sgn}(\varepsilon_h)}{v_0(E)} f_{-\sigma,\sigma}(\frac{\alpha\ell(E)}{1 - \alpha\ell(G_0(E))}, \frac{\alpha\ell(E)}{1 - \alpha\ell(G_0(E))}) .$$

for the fraction of $\eta = N_M/N_C$ of impurities per carbon atom. Couplings $\alpha_{\ell}(E)$ are given by Eq. (1), $G_0(E)$ and $v_0(E)$ are graphene’s Green function and DOS per atom and spin, and auxiliary function $f_{-\sigma,\sigma}(x,y)$ is,

$$f_{-\sigma,\sigma}(x,y) = \frac{1}{2} \delta_{\sigma,\sigma'} |x|^2 + \frac{1}{8} |x + (\sigma - \sigma') y|^2 .$$

The spin-flip rate $1/\tau_s$ is peaked at resonances where denominators $1 - \alpha_{\ell}(E) G_0(E)$ have minima.

Spin relaxation rate $1/\tau_s$ is plotted in Fig. 2 which is the main result of this paper. Zero temperature rate shows singlet and triplet split resonance peaks, with widths $\Gamma$ of about 20 and 40 meV, respectively. At 300 K the peaks merge. In realistic samples the neutrality point fluctuates due to electron-hole puddles [34, 35]. Also, different magnetic impurities would give different peak positions and widths, providing additional broadening. All such effects are modeled by gaussian energy broadening with standard deviation $\sigma_{br}$. In Fig. 2 we use $\sigma_{br} = 110$ meV. From Fig. 2(b) we can conclude that the temperature dependence of $1/\tau_s$ is rather weak, essentially given by Fermi broadening of the resonance structure. Finally, in Fig. 2(c) we compare the calculated spin relaxation rates with experiment, with adjusted $\eta$. The agreement is remarkable. In fact, one can find a nice agreement for a large window of $J$ (see [32]) by adjusting $\sigma_{br}$ and $\eta$. Vacancies and different adatoms are well covered by this mechanism.

In [32] we plot $1/\tau_s$ for ferromagnetic $J = 0.4$ eV. The only effect, after broadening, is the opposite (slight) skewness of the energy dependence (keeping $\varepsilon_h$ unchanged), coming from the flipped positions of the singlet and triplet peaks. Also, in [32] we demonstrate that resonance enhancement of $1/\tau_s$ is present for even much smaller $J$, as long as $J > \Gamma$, confirming the intuitive picture of the enhancement coming from the spin precession being faster than the leakage rate. One important conclusion one can draw from this concerns spin-orbit coupling (SOC). Hydrogen adatoms induce SOC of about 1 meV [31, 37]. This is smaller than $\Gamma$, so the resonant enhancement will be much less pronounced, unless $\eta$ is increased to, say $10^{-3}$ [32]. Nevertheless, there could be heavier adatoms that induce both large spin-orbit coupling and resonant scattering so that resonance enhancement could be present. It was recently shown that Si adatoms sitting on top of the carbon bonds could also give 100 ps spin-flip times [21], but for concentrations of $\eta \sim 10^{-3}$, three orders more than what is needed for magnetic resonant scatterers. It is possible that the mechanism is indeed resonance enhancement of the spin-flip rates. In fact, resonant scattering by spin-orbit coupling inducing impurities was already invoked to explain strong spin-flip scattering in alkali [38] and noble [39] metals.

There have already been spin relaxation experiments with hydrogenated graphene. According to our theory,
an \( sp^3 \) bonded hydrogen should increase the spin relaxation rate. Unfortunately, the experimental results differ. In Ref. [30] the spin relaxation rate decreased upon hydrogenation. In Ref. [37] spin relaxation has not changed much, while in Ref. [29] evidence for magnetic moments was provided based on a different model, that of fluctuating magnetic fields. It is likely that the experimental outcomes depend on the hydrogenation method. At present it is not possible to form a unique experimental picture with which we could gauge our theory. But we stress that we use hydrogen only as a convenient model to formulate our mechanism quantitatively. The Hamiltonian we use is rather generic, and the results are very robust as far as the details in \( J \) and other parameters are concerned. It is even possible that hydrogenation isolates existing magnetic moments at vacancies, thereby increasing \( \tau_s \), as seen in Ref. [34].

Resonant spin-flip scattering in a one-dimensional double-barrier atomic chain. To make the resonant enhancement of the spin relaxation rate more transparent, we introduce a toy model that captures all the essential features. Consider an atomic chain with lattice constant \( b \), whose central site (\( m = 0 \)), trapped within two \( \delta \) barriers on its nearest neighbors, hosts the exchange interaction \( J \hat{s} \cdot \hat{S} \). The hopping Hamiltonian is

\[
H = -t \sum_{\langle m,n \rangle} (c_m^\dagger c_n + c_n^\dagger c_m) + U \sum_{m = \pm 1} c_m^\dagger c_m - J \hat{s} \cdot \hat{S}, \tag{9}
\]
as sketched in the inset of Fig. 3(a). In the singlet-triplet basis the transmission and reflection amplitudes \( \gamma_{\ell,m \ell}(k) \) and \( \beta_{\ell,m \ell}(k) \), are obtained analytically as

\[
\gamma_{\ell,m \ell}(k) = \frac{-2it(1 + Ue^{ikb})^{-1}}{[Ek + J(4\ell - 3)](1 + Ue^{ikb}) + 2te^{ikb}}, \tag{10}
\]
\[
\beta_{\ell,m \ell}(k) = \gamma_{\ell,m \ell}(k) - \frac{t + Ue^{-ikb}}{t + Ue^{ikb}}. \tag{11}
\]
The energy of the incident electron of momentum \( k \) is \( E_k = -2t \cos(k) \), and the composite (electron and impurity) spin state \( | \ell, m_\ell \rangle \), with angular momentum \( \ell = 1 \) for triplet and \( \ell = 0 \) for singlet states; \( m_\ell \) is the corresponding angular momentum projection (this index is dropped in what follows, as neither amplitude depends on it). We are interested in the transmission \( t = |\gamma|^2 \) and reflection \( r = |\beta|^2 \) probabilities of various spin transition processes \( \sigma \rightarrow \sigma' \) so we trace out the impurity spin. The result is

\[
t(E_k)_{\sigma,\sigma'} = f_{\sigma,\sigma'}(\gamma_1(k), \gamma_0(k)), \tag{12}
\]
\[
\tau(E_k)_{\sigma,\sigma'} = f_{\sigma,\sigma'}(\beta_1(k), \beta_0(k)), \tag{13}
\]
where function \( f_{\sigma,\sigma'} \) is given by Eq. (8). The above results are shown in Fig. 3(a). We plot the ratio \( R(E) \) of spin flip versus spin-conserving probabilities \( R(E) = \frac{[t(E)_{\sigma,-\sigma} + r(E)_{\sigma,-\sigma}]}{[t(E)_{\sigma,\sigma} + r(E)_{\sigma,\sigma}]} \) for different \( j/t \). For \( j/t = -0.5 \) and \( -0.05 \), i.e., when \( t^2/U^2 \lesssim j/t \), spin-flip transitions are as likely as the spin-conserving ones. For smaller \( j/t \), spin-flip probabilities become proportional to \( j^2 \), reaching the usual perturbative regime.

Pronounced resonances appear for \( U \gg t \). In this limit the singlet and triplet resonant energies are \( E_{res,\ell} \approx -2t^2/U - j(4\ell - 3), \) and \( \Gamma \approx t^3/4U^2 \) is the resonance width. The dwell time \( \Delta t_{dw} = \hbar/\Gamma \) is much greater than the hopping time \( \hbar/t \). We further assume that \( \Gamma \ll j \), which is the limit of resonant enhancement of spin relaxation rate. This condition means that the electron has enough time to precess by the exchange field before leaking out of the well. The singlet and triplet resonance peaks are well resolved in this limit. Equation (12) now gives Lorentzian,

\[
t(E)_{\sigma,\sigma'} \approx \sum_{\ell=0,1} \frac{(4\ell \delta_{\sigma,\sigma'} + 1)^3 t^6/2U^4}{(E - E_{res,\ell})^2 + 4t^6/5U^4}. \tag{14}
\]
and similarly Eq. (13) the reflectivities: \( t_{\sigma,-\sigma} = t_{\sigma,-\sigma} \), and \( t_{\sigma,\sigma} = 1 - t_{\sigma,-\sigma} - t_{\sigma,\sigma} - t_{\sigma,-\sigma} \). Figures 3(b) and 3(c) show the comparison of the exact and above approximate formulas for \( j/t = -0.05 \). The peak positions depend on \( j \) via \( E_{res,\ell} \), but the values at maxima are \( j \)-independent. At resonances the spin-flip to spin-conserving probabilities come as \( 1/3 \), see Fig. 3(a): 25% of scattered electrons change spin. The reason is that a spin up electron forms triplet state \( |1,1 \rangle \) with 50% chance, \( |1,0 \rangle \) and \( |0,0 \rangle \) with 25%. The chance that the electron flips its spin is 50% for each \( |1,0 \rangle \) and \( |0,0 \rangle \) states. This gives the 25% probability for a spin-flip, as we see at resonances.
In [32] we show, using our 1d model, that an impurity sitting at the barrier site and not inside the well, does not have such a pronounced effect on the spin-flip probability, justifying our exchange model of hydrogen on graphene that places $J$ on the hydrogen site only.

In conclusion, we propose that resonant scattering by magnetic impurities in graphene, caused by vacancies or adatoms, causes the observed fast spin relaxation rates. Resonant enhancement of exchange interaction, but also of the weaker spin-orbit coupling, opens new prospects for investigating impurity magnetic moments, dynamical polarization of impurity spins, Kondo physics, and resonant scattering in graphene.

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Density functional theory [1] has been used to calculate the electronic structure of hydrogenated graphene in the supercell approach. We used the generalized gradient approximation for the exchange-correlation functional [2]. The atomic positions in the supercell calculations have been relaxed using the quasi-newton algorithm based on the trust radius procedure implemented within the plane wave pseudopotential code Quantum ESPRESSO [3]. For the atomic species we have used ultra-soft pseudopotentials [4, 5] with PBE exchange-correlation functional [2] with kinetic energies cut-offs of 30 Ry for the wave function and 300 Ry for the density. The vacuum of 15 Å to separate the hydrogenated graphene planes has been used. We found that the covalent C-H bond length \( d_{CH} \) is close to 1.13 Å. Next-nearest distance \( d_{CH} \) between the three closest carbon atoms to the hydrogenated carbon, a tetrahedral edge length, is 2.516 Å. The hydrogen bonding distorts the graphene plane by pulling the hydrogenated carbon atom out of plane by about 0.36 Å.

The relaxed structure was then used in the full-potential spin-polarized self-consistent calculations using the linearized augmented plane wave (FLAPW) method as implemented in the FLEUR code [6] in the film mode. We used the cut-off parameter for the plane wave expansion \( k_{\text{max}} = 4.7 \text{ bohr}^{-1} \) and 64 \( k \)-points in the irreducible wedge of the Brillouin zone. The muffin-tin radii for carbon of 1.32 bohr and for hydrogen 0.81 bohr were used.

Spin relaxation rate.

The spin relaxation rate is obtained by formulating rate equations. Suppose we have an electron spin accumulation in graphene described by the spin \( (\sigma) \)-dependent chemical potential \( \mu_{\sigma} \). The electron distribution functions differ from equilibrium as \( f_{\sigma\alpha} = f_{\sigma} + \delta f_{\sigma\alpha} \), where

\[
\delta f_{\sigma\alpha} \approx \left( -\frac{\partial f_{\sigma}}{\partial \varepsilon_k} \right) (\mu_{\sigma} - \varepsilon_F).
\]  

We denoted as \( f_{\sigma} = f^{0}(\varepsilon_k) \) the Fermi-Dirac function, \( \varepsilon_k \) the electron energy, and \( \varepsilon_F \) the Fermi level. The electron spin is

\[
s = \sum_k \left( \frac{\partial f_{\sigma}}{\partial \varepsilon_k} \right) \mu_{\sigma},
\]

with \( \mu_{s} = \mu_{\uparrow} - \mu_{\downarrow} \). The spin relaxation rate is defined from equation,

\[
\frac{\partial s}{\partial t} = \sum_k \left( \frac{\partial f_{\sigma}}{\partial \varepsilon_k} \right) \frac{\partial \mu_{\sigma}}{\partial t} \equiv -\frac{s}{\tau_s}.
\]

Let \( W_{k\sigma\uparrow|k'\sigma'\downarrow} \) be the spin-flip rate, that is, the rate of the transition of an electron with momentum \( k \) and spin up (\( \uparrow \)), in the presence of an impurity with spin down (\( \downarrow \)), to another state of momentum \( k' \) and spin down (\( \downarrow \)), and impurity spin up (\( \uparrow \)) (the electron and impurity spins are flipped). Let the probability of the impurity spin being up (\( \uparrow \)) and spin down (\( \downarrow \)) be \( p_\uparrow = 1/2 \), and using the symmetry of the spin-flip rates, we get

\[
\frac{\partial f_{k\uparrow}}{\partial t} = -\frac{1}{2} \sum_{k'} W_{k\uparrow|k'\downarrow} \left( f_{k\uparrow} - f_{k'\downarrow} \right).
\]

Similarly for the rate of \( f_{k\downarrow} \), we can then write

\[
\frac{\partial s}{\partial t}\text{.}
\]

Substituting the spin accumulation and comparing with the defining equation for \( \tau_s \) we get

\[
\frac{1}{\tau_s} = \sum_{k,k'} \left( -\frac{\partial f_{\sigma}}{\partial \varepsilon_k} \right) W_{k\sigma\uparrow|k'\sigma'\downarrow}. 
\]

This equation is used to evaluate the temperature-dependent spin relaxation rates in the paper.

Finally, the transition rates in the presence of \( N_A \) impurities are calculated from the T-matrix,

\[
W_{k\sigma\Sigma|k'\sigma'\Sigma'} = N_A \frac{2\pi}{\hbar} |T_{k\sigma\Sigma|k'\sigma'\Sigma'}|^2 \delta(\varepsilon_k - \varepsilon_{k'}). 
\]

All what is necessary for spin-flip rates is to transform the singlet and triplet T-matrix amplitudes, Eq. (5) in the paper, via composite spin states \( |\uparrow\downarrow\rangle \) and \( |\downarrow\uparrow\rangle \). This is a place where the function \( f_{\sigma\sigma'}(x,y) \), Eq. (8) in the main text, enters the game.
carrier density \[ \times 10^{12} \text{cm}^{-2} \]

This lower value of \( J \) is expected that if \( J < m \Gamma \), the ratio \( \tau / \tau_s \) decreases as \( J^2 \) with decreasing \( J \). This is evident in Figs. 3 and 4. This is also the regime of spin-orbit coupling. Say, if an adatom induces local spin-orbit coupling of 1 meV, which is reasonable, then resonance scattering would enhance the spin-orbit spin relaxation rate roughly as \( 1/16 \) \( (1/4^2) \) compared to what is shown in Fig. 3 (which is for \( |J| = 4 \) meV). For a 1 ppm of adatoms the spin relaxation time would be 10-100 nanoseconds. The experimental rates could then be achieved by \( \eta = 10^{-3} - 10^{-4} \) spin-orbit coupling inducing resonant adatoms.

**Double-barrier atomic chain with a local moment sitting off the resonant site.**

In the paper we state that it is intuitively clear that the exchange coupling on the resonant site dominates spin-flip processes, so we can neglect \( J \) on the carbon atoms near hydrogen. We can see this explicitly on our atomic chain model. Suppose a local spin giving exchange \( J \) sits not inside resonant well but at one of the barriers, say the left one, i.e. \( m = -1 \). The model Hamiltonian is as follows:

\[
H_{\text{off}} = -t \sum_{(m,n)} (c_{m}^\dagger c_{n} + c_{m}^\dagger c_{n}^\dagger) + \sum_{m=1}^{\mp 1} \sum_{n=0}^{\pm 1} (U c_{m}^\dagger c_{m} - J \delta_{m,\mp 1} \hat{S}).
\]
Transmissions and reflections amplitudes $\gamma_\ell$ and $\beta_\ell$ can be calculated to be,

$$
\gamma_\ell = \frac{-e^{-\epsilon_{kkb}} + e^{\epsilon_{kkb} Y_\ell}}{e^{\epsilon_{kkb}} + \frac{\epsilon_{kkb}}{t+\epsilon_{kkb}} [1 + e^{\epsilon_{kkb} U/t}] + e^{\epsilon_{kkb} X_\ell}},
$$

$$
\beta_\ell = \gamma_\ell X_\ell - Y_\ell,
$$

where auxiliary functions $X_\ell$ and $Y_\ell$ are,

$$
X_\ell = \frac{t + e^{\epsilon_{kkb} U}}{t + e^{\epsilon_{kkb} [U - (4\ell - 3)J]}},
$$

$$
Y_\ell = \frac{t + e^{-\epsilon_{kkb} [U - (4\ell - 3)J]}}{t + e^{\epsilon_{kkb} U [U - (4\ell - 3)J]}}.
$$

Figure 5 shows main characteristics of $H_{\text{int}}$, Eq. (9), which allows us to call this model as off-resonant. Panel 5(a) provides the ratio $R(E)$ for spin-flip versus spin-conserving probabilities, i.e.,

$$
R(E) = \left[ t(E)_{\sigma,-\sigma} + t(E)_{\sigma,-\sigma} \right] / \left[ t(E)_{\sigma,\sigma} + t(E)_{\sigma,\sigma} \right]
$$

for different $J/t$. It is obvious when comparing with Fig. 3(a) in the main text that spin-flip processes are significantly suppressed. Figure 5(b) shows transmission and reflection probabilities $t(E)_{\uparrow,\uparrow}$ and $t(E)_{\downarrow,\downarrow}$ for $J/t = -0.05$ (to be visible, they are magnified by factor 10); the dotted line on the background is the transmission probability for the local moment on the resonant site inside the well (see Fig. 3(b) in the main text). Clearly, the spin-flip transitions are much more inhibited than in the resonant case discussed in the paper, justifying neglecting the off-resonant site exchange, especially when energy fluctuations from puddles wash out the fine structure of the resonant peaks. Figure 5(c) shows $t(E)_{\uparrow,\uparrow}$ (solid line) and $t(E)_{\uparrow,\downarrow}$ (dashed line) for $J/t = -0.05$. Similarly, the dotted line represents transmission probability $t(E)_{\uparrow,\uparrow}$ in the resonant case.

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