Electrical spin manipulation in graphene nanostructures

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We propose a mechanism to drive singlet-triplet spin transitions, electrically, in a wide class of graphene nanostructures that present pairs of in-gap zero modes, localized at opposite sublattices. Examples are rectangular nanographenes with short zigzag edges, armchair ribbon heterojunctions with topological in-gap states and graphene islands with sp³ functionalization. The interplay between the hybridization of zero modes and Coulomb repulsion leads to symmetric exchange interaction that favors a singlet ground state. Application of an off-plane electric field to the graphene nanostructure generates an additional Rashba spin-orbit coupling, which results in antisymmetric exchange interaction that mixes $S = 0$ and $S = 1$ manifolds. We show that modulation in time of either the off-plane electric field or the applied magnetic field permits to perform electrically driven spin resonance in a system with very long spin relaxation times.

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1. On account of their finite size, they have a gapped spectrum, except for two single-particle in-gap states, that we label $\psi_{\pm}$, and host two electrons (see figure 2(b)).

2. The wave function of these in-gap states turns out to be a linear combination of two zero mode states that are mostly localized in one of the sublattices, labeled $A$ and $B$ that form the honeycomb lattice (figure 2(d, e, f, g)). We refer to these zero mode states as $\psi_A$ and $\psi_B$.

3. The overlap of $\psi_A$ and $\psi_B$, and thereby the bonding-antibonding splitting ($\delta \equiv \epsilon_+ - \epsilon_-$) of the single-particle spectrum, depends on the geometrical properties of the graphene structure, and is therefore an important design parameter (figure 2(c)).

4. The electronic ground state is a singlet with $S = 0$, the first excited state is a triplet $S = 1$ and their energy separation $J$ is proportional to $\delta^2/\tilde{U}$, where $\tilde{U}$ is the Coulomb energy overhead of adding a second electron in the localized states ($\psi_{A,B}$).

In this work two things are done. First, we provide a quantum theory, beyond mean field approximation, for the spin states and the exchange $J$ in this class of graphene nanostructures. Second, we study how the application of an off-plane electric field generates a Dzyaloshinskys-Moriya (DM) antisymmetric exchange that could be used to enable spin transitions between the ground state singlet and the states in the triplet. Importantly, these transitions are strictly forbidden, in the absence of DM interaction, in conventional electron-paramagnetic resonance experiments, where both spins interact with a dc field $B_0$ and a perpendicular $ac$ field $B_{ac}$ and only transitions that conserve $S$ may be induced. Therefore, our results pave the way towards electrically driven spin res-
onance in graphene nanostructures, complementing recent experiments on electrically detected spin resonance in graphene.\textsuperscript{19,20}

Graphene zero modes with a wave function localized in a single sublattice were predicted to occur in zigzag graphene edges\textsuperscript{21,22} and around carbon atoms with sp\textsuperscript{3} functionalization.\textsuperscript{23–26} Their direct experimental observation, by means of scanning tunneling microscopy, has been reported both for the edge states of rectangular nanographenes with short zigzag edges\textsuperscript{27,28} as well as for individual and for pairs of chemisorbed hydrogen atoms in graphene.\textsuperscript{27,28} These sub-lattice polarized zero modes are expected to host unpaired spin electrons, giving rise to the formation of local moments.\textsuperscript{22,26,29–36} Sublattice polarized zero modes have recently been predicted to exist as in-gap topological states at the interface of certain graphene ribbons with armchair edges, shown in figure 1(b). Recent progress in fabrication of graphene ribbon heterojunctions\textsuperscript{16,38} shows that fabrication of this type of structure is not out of reach of state of the art in nanographene synthesis.

The exploration with STM of some of the graphene nanostructures studied here has been demonstrated.\textsuperscript{15,16,28} With this approach, the application of an off-plane electric field significantly larger than in conventional field effect transistor geometries is possible. On the other hand, STM can be used to carry out electrically driven spin paramagnetic resonance of individual atoms\textsuperscript{39–41} and coupled spin 1/2 atoms.\textsuperscript{42} Therefore, the electrical manipulation of localized spin states in graphene seems within reach with state of the art surface scanning probes.

**Modeling.** We model the single particle states of the graphene nanostructures both with the standard one-orbital tight-binding model, with first neighbor hopping $t = 2.7$ eV. Electron-electron interactions are treated with the Hubbard model, both at the mean field approximation, including all the single particle states, or exactly for the subspace of 2 electrons and 2 orbitals that controls the spin properties of the studied systems. In the case of graphene nanostructures, it is well known that mean field Hubbard model calculations and density functional calculations give very similar results.\textsuperscript{22,24} The spin orbit coupling effect considered in the following will be of Rashba type\textsuperscript{44–46} that can be externally modulated with an electric field.

The non-interacting spectrum. A scheme of the single-particle spectrum characteristic of the gapped graphene with 2 in-gap states is shown in figure 2(b). The energies and wave-functions of the in-gap states are denoted by $\epsilon_{\pm}$ and $\psi_{\pm}$ respectively. It is always possible to write down the wave function of a couple of conjugate states, with single-particle energy $E$ and $-E$, in terms of the same sublattice polarized states $\psi_A$ and $\psi_B$. Therefore, we write

$$\psi_A(i) = \frac{1}{\sqrt{2}} (\psi_+(i) + \psi_-(i))$$

$$\psi_B(i) = \frac{1}{\sqrt{2}} (\psi_+(i) - \psi_-(i))$$ (1)

In the case of the in-gap states, the peculiar property of the resulting $\psi_A$ and $\psi_B$ is that they are spatially separated. As a result, the resulting splitting that arises from the hybridization of the zero modes,

$$\delta = 2 \langle \psi_A | H_0 | \psi_B \rangle \equiv 2\tilde{t}$$ (2)

turns out to be small. In figure 2(c) we plot $\delta$ for different nanographenes as a function of the spatial separation between the zero modes. It is apparent and well known\textsuperscript{21} that this quantity decays exponentially with $W$.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{Three types of graphene nanostructures that host pairs of zero modes localized in opposite sublattices. a) Rectangular graphene nanoribbons with short zigzag edges that host 1 unpaired electron each. b) Armchair graphene heterojunctions, hosting 1 zero mode at each interface. c) Graphene nanoisland with sp\textsuperscript{3} functionalization (chemisorbed atomic hydrogen). In the three cases, the green arrows represent the magnetization calculated with a mean field Hubbard model.}
\end{figure}
FIG. 2: a) Graphene nanoribbon with $W = 7$. b) Sketch of the single-particle energy spectrum for the graphene nanostructures shown in figure 1. A gap, separating the doubly occupied states from the empty states, contains 2 in-gap states, $\epsilon_\pm$, split by $\delta = \epsilon_+ - \epsilon_-$. c) Dependence of $\delta$ on the distance between both for edge and interface states. The splitting arises from the hybridization of the zero modes, $\psi_A$ and $\psi_B$, for the ribbons (d, e) and heterojunctions (f, g) (see equation (2)).

In the limit where $W$ is very large (see figure 2(c)), $\delta$ vanishes, and the energy of the in-gap states goes to $E = 0$, showing that these sublattice polarized states are zero modes.

Our next task is to demonstrate that in-gap states in these structures hold local moments. This has been established, using either DFT and/or mean field Hubbard model calculations, in the case of infinitely long graphene ribbons with zigzag edges, as well as the small nanoribbons considered here, and also for hydrogenated graphene. To the best of our knowledge, the emergence of local moments in the case of undoped topological junctions has not been explored yet. We therefore carry out a mean field Hubbard model calculation (see supplementary material for details) to address the emergence of local moments associated to the topological in-gap states and, for comparison, the well understood case of graphene nanoribbons. For the topological in-gap states, we consider a structure with periodic boundary conditions and two interfaces, that accommodate one in-gap state each. For $U = t = 2.7 \text{eV}$, we find broken symmetry solutions with a finite local magnetization, $M(i) = \langle S_z(i) \rangle$ that is mostly located in the region where either $\psi_A$ or $\psi_B$ are non-zero, for all structures except those where $\delta$ is large (i.e., those where $\psi_A$ and $\psi_B$ are strongly hybridized). This applies both for heterojunctions and nanoribbons. In the mean field approximation, the transition between non-magnetic and broken symmetry transitions is abrupt. The mean field broken symmetry solutions have lower energy for antiferromagnetic (AF) correlations between spins in opposite sublattices, that result in a total zero magnetic moment $\sum_i M(i) = 0$ (see figure 1(b)). Solutions with a net magnetic moment and ferromagnetic (FM) correlations between opposite sublattices have higher energy and $\sum_i M(i) = 1$, as expected for a $S = 1$ configuration in two antiferromagnetically coupled $S = 1/2$. 
We study the exchange energy as the difference between FM and AF solutions $J_{MF} = E_{FM} - E_{AF}$ for several different nanographenes, both for the edge and interface states. We find that, for the same value of $W$, the exchange is larger for ribbons than heterojunctions. This ultimately arises from the larger hybridization of the edge zero modes, compared with the topological interface zero modes (see figure 2(c)). We show in figure 3 that $J_{MF}$ can be as large as 40 meV for graphene ribbons, and be made as small as necessary by increasing the distance $W$ between the zero modes. Importantly, as we show in figure 3(b), we find that, both for ribbons and heterojunctions, exchange energy scales as

$$J_{MF} \propto \frac{t^2}{U}$$

where

$$\tilde{U} = U \sum_i |\psi_A(i)|^2 = U \sum_i |\psi_B(i)|^2 = U \eta$$

is the average addition energy for these states, as computed in the Hubbard model (see supplementary material) and $\eta$ is the inverse participation ratio of the zero mode states. This scaling provides a strong indication that the mechanism of antiferromagnetic interaction is kinetic exchange, that arises naturally for half-filled Hubbard dimers. Our calculations show that, for a given type of structures (ribbon or heterojunction), the inverse participation ratio $\eta$ is quite independent of $W$. Thus, for the zigzag edge zero modes we find $\eta \approx 0.1$ and for the topological in-gap states we find $\eta \approx 0.035$. The smaller $\eta$ for the heterojunction states can be anticipated, as they can spread at both sides of the junction, in contrast with the edge states.

All these results, most notably the scaling of equation 3, strongly suggest that magnetic correlations are governed by the two electrons that occupy the two in-gap states. This is also the case for graphene ribbons with infinitely long zigzag edges. In order to go beyond the mean field picture and to be able to describe local moments in these nanographenes with a full quantum theory without breaking symmetry, we restrict the Hilbert space to the configurations of 2 electrons in the two zero modes. To do so, we represent the Hubbard interaction in the one body basis defined by the states $\psi_A$ and $\psi_B$. The Hamiltonian so obtained is a two site Hubbard model with renormalized hopping and on-site energy:

$$\mathcal{H}_{\text{eff}} = \tilde{t} \sum_{\sigma} \left( a_\sigma^\dagger b_\sigma + b_\sigma^\dagger a_\sigma \right) + \tilde{U} \left( n_{A\uparrow} n_{A\downarrow} + n_{B\uparrow} n_{B\downarrow} \right)$$

where $a_\sigma = \sum_i \psi_A(i) c_\sigma^\dagger$ and $b_\sigma = \sum_i \psi_B(i) c_\sigma^\dagger$ are the operators that create an electron in the zero modes $\psi_A$ and $\psi_B$ with spin $\sigma$, respectively. In turn, $n_{A,\sigma} = a_\sigma^\dagger a_\sigma$ is the number operator for the $\psi_A$ state with spin $\sigma$. In addition, we consider the Zeeman coupling to a magnetic field,

$$\mathcal{H}_Z = g \mu_B \sum_{\sigma,\sigma'} \tilde{B} \cdot \hat{S}_{\sigma,\sigma'} \left( a_\sigma^\dagger a_{\sigma'} + b_\sigma^\dagger b_{\sigma'} \right)$$

where $\hat{S}_{\sigma,\sigma'}$ are the $S = 1/2$ spin matrices, $g = 2$ is the gyromagnetic factor and $\mu_B = \frac{e}{2m_e} T - 1$ is the Bohr magneton.

Hamiltonian is a two-site Hubbard model, where the sites correspond to the zero mode states $\psi_{A,B}$, shown in figure 2(b, c, d, e). This model can be solved analytically or by a straightforward numerical diagonalization (see supplementary material). For the relevant case of 2 electrons, the dimension of the Hilbert space is 6 and the ground state is always a singlet. We are interested in the limit $\tilde{t} \ll \tilde{U}$. A cartoon of the spectrum is shown in figure 4(a). In that case the excited state manifold is a triplet, way below two excited singlets that describe states with double occupation of the zero modes.

Unlike the mean field solution, the exact solution of Hamiltonian has no abrupt change of behavior from non-magnetic to magnetic solutions. However, depending on the ratio $\tilde{t}/\tilde{U}$, the physical properties of the system are very different. This is quantified by the weight on the ground state wave function of the states where 2 electrons occupy one zero mode, denoted by $P_2$. For $U = 0$ the ground state is a trivial singlet, formed by two electrons in the lowest energy in-gap state and $P_2 = 0.5$. For very small $\tilde{t}/\tilde{U}$, $P_2$ goes to zero. For a fixed value of $t$ and $U$, the effective hopping $\tilde{t}$ is controlled by the dimensions of the nanographene structure. Thus, in figure 5(a), we
show $P_2$ for a nanoribbon, assuming $U = t$, as a function of the ribbon width $W$. We see that for $W > 9$, the weight of the double occupancy configurations is smaller than 5 percent of the state, and the charge fluctuations are effectively frozen. In that limit, it is well known\(^{15,54}\) that the four lowest levels in the model of equation (5) can be mapped into the Heisenberg Hamiltonian:

$$\mathcal{H}_{\text{Heis}} = J_H \vec{S}_A \cdot \vec{S}_B$$

(7)

where $\vec{S}_{A,B}$ are the spin $\frac{1}{2}$ operators describing the electronic spins localized in states $\psi_A$ and $\psi_B$, respectively and $J_H \simeq \frac{4e^2}{a^2 U}$. The Hamiltonian of equation (7) has a ground state singlet ($S = 0$) and an excited state triplet with $S = 1$, separated in energy by $\Delta = E(S = 1) - E(S = 0) = J_H$ (see figure 4(b)). Heterojunctions. Effectively, the upper limit to $J_H$ is marked by the crossover to the un-correlated regime, where double occupancy $P_2$ is not negligible. On the other side, $J$ can be made exponentially small when the distance between the two zero modes is increased.

We now consider the effect of spin-orbit interactions induced by an off-plane electric field, $\vec{E}$, on the spin dynamics of these 4 states. These can be described with a Rashba spin-orbit coupling\(^{13,15}\),

$$\mathcal{H}_R = it_R \sum_{\sigma,\sigma',\langle i,j \rangle} \vec{E} \cdot \left( \vec{d}_{ij} \times \vec{\sigma}_{\sigma,\sigma'} \right) c_{i\sigma}^\dagger c_{j\sigma'}$$

(8)

where $\langle i,j \rangle$ labels first neighbors and $\vec{d}_{ij}$ in the vector linking them. $\sigma = \pm$ labels the eigenstates of the spin matrix $S_z$, $\vec{\sigma}_{\sigma,\sigma'}$ are the Pauli matrices (with eigenvalues $\pm 1$), and the $c$ and $c^\dagger$ are second quantization fermionic operators. The extrinsic spin-orbit coupling constant $t_R$ is zero unless an off-plane electric field is applied $E_{\text{applied}} \hat{z}$ to break mirror symmetry\(^{15}\):

$$t_R = \frac{e E_{\text{applied}}}{V_{\text{applied}}} \xi$$

(9)

where $e$ is the electron charge, $E_{\text{applied}}$ is the voltage drop across atomically thin graphene, $\xi = 6 \text{meV}$ is the spin orbit coupling of carbon and $V_{\text{applied}}$ is the hybridization between $p$ and $s$ orbitals\(^{15}\).

For an electric field $E = 50 \text{Volt}/300 \text{nm}$, standard for graphene field effect transistors\(^{32}\) we have $t_R \simeq 3.7 \text{meV}$\(^{55}\). Importantly, with an STM tip it is possible to apply a few volts at 1 nm, so that $t_R = 100 \text{µeV}$ could be reached.

The Rashba spin-orbit Hamiltonian adds an spin-flip hopping in the 2-site model (5):

$$\mathcal{V}_R = \sum_{\sigma} \left( \tilde{t}_R(\sigma) a_{i\sigma}^\dagger b_{\sigma} + \tilde{t}_R(\sigma)^* b_{\sigma} a_{i\sigma} \right)$$

(10)

where $\sigma = -\sigma$ and

$$\tilde{t}_R(\sigma) = \sigma \langle \psi_{A\sigma} | \mathcal{V}_R | \psi_{B\sigma} \rangle \equiv \sigma t_{R}$$

(11)

For the graphene nanostructures considered here, we find that $t_R$ is real. Unexpectedly, we find that $\tilde{t}_{R\sigma}$ is always more than 5 times larger than $t_{R\sigma}$. The origin of the enhancement of the Rashba interaction in graphene nanostructures has to do with a constructive interference between the modulation of the sign of the in-gap zero modes states and the angle-dependence sign of the Rashba hopping.

The addition of this spin-flip hopping to the Hubbard model results, in the strong coupling limit $U \gg t$, in two types of additional terms to the effective spin Hamiltonian\(^{13,55}\):

$$\mathcal{V}_\text{DM} = J_{\text{DM}} \left[ (S_{A\sigma} S_{B\sigma} - S_{A\sigma} S_{B\sigma}) + (S_{A\sigma} S_{B\sigma} - S_{A\sigma} S_{B\sigma}) \right]$$

(12)

$$\mathcal{V}_\text{anis} = J_{s} S_{A\sigma} S_{B\sigma}$$

(13)

with $J_{\text{DM}} = \frac{s t_R}{U}$ and $J_s = \frac{e^2}{4} t_R^2$.

The first term (equation (12)) is the widely studied anisotropic exchange postulated by Dzyaloshinsk\(^{12}\) and derived by Moriy\(^{51}\). It does not conserve $S_z$. The physical origin is transparent: exchange arises from the virtual hopping of one electron between states $\psi_A$ and $\psi_B$. This hopping occurs through a spin conserving channel, with amplitude $t_R$ and through a spin-flip channel $\tilde{t}_R$. Thus, two hoppings through the same channel, either spin conserving or spin flip, preserve the spin of the electron. In contrast, the crossed term, by which only one hopping preserves the spin, results in an effective interaction that does not conserve $S_z$. This is the DM interaction, which is the dominant addition coming from the Rashba perturbation, given that $t_R \gg \tilde{t}_R$.

The DM interaction scales with the kinetic exchange as $J_{\text{DM}} = \frac{t_R}{U} J$. Thus, $J$ is in the range of $\text{meV}$, so that $J_{\text{DM}}$ in this system is, at most, in the $\mu\text{eV}$. Whereas this is a small energy scale, it has a qualitatively important consequence: it permits otherwise forbidden transitions between singlet and triplet manifolds. This is shown in figure 4(b), where we plot the spectrum of the 2-site Hubbard model, as a function of the off-plane magnetic field $B$, for a ribbon with $W = 10$, chosen so that for a moderate magnetic field the Zeeman splitting of the triplet manifold offsets the singlet-triplet splitting $J$. The calculation is done including the effect of the Rashba interaction. The effect of the small Rashba interaction is only apparent when the $S_z = -1$ triplet state gets close in energy to the $S = 0$ ground state. In the absence of Rashba interaction, these two spectral lines would cross each other.

We have verified that dipolar interactions (see supplementary material\(^{15}\)) are small (for the $W = 10$ nanoribbon, $10^{-2} \mu\text{eV}$). Importantly, they produce an anisotropic symmetric exchange that does not couple $S = 0$ with the $S_z = \pm 1$ states. In addition, dipole interaction can not be modulated electrically in this class of systems.
The states $S_z = -1$ from the triplet and the $S = 0$ define a two level system with Hamiltonian:
\[ \mathcal{H}_{\text{TLS}} = \frac{1}{2} \hbar \omega_0 (\tau_z + 1) + \frac{1}{2} \hbar \Omega \tau_x \]  
(14)
where $\tau_z$ and $\tau_x$ are the $S = 1/2$ Pauli matrices (with eigenvalues $\pm 1$). $\hbar \omega_0 = J - g_\mu_B B$ is the splitting of the two levels when the electric field is zero, and
\[ \hbar \Omega \propto \frac{\tilde{I}}{U} \tilde{I}_R \]  
(15)
is the Rabi coupling. As expected from equations \[ \text{[10]} \text{ and [15]}, \] we find that $\hbar \Omega$ scales linearly with the electric field (figure 4(d)). It must be noted that our TLS is different from the case of singlet-triplet qubits where both states have $S_z = 0$. As a result, the energy difference can be tuned with a magnetic field, but this also removes the protection against fluctuations of the magnitude of the external magnetic field that makes singlet-triplet qubits convenient \[ \text{[9]}. \]

The energy scale $\hbar \Omega$ defines a Rabi coupling between the spin split levels. In order to assess its magnitude, we first compare it with the Rabi coupling achieved by pumping a spin $S = 1/2$ system with the ac magnetic field of a microwave. The magnetic field of a microwave generated in pulsed state of the art ESR setup is, at most, $B_{ac} = 4 \text{mT}$, leading to a Rabi splitting of $g_\mu_B B_{ac} \approx 0.4 \mu\text{eV}$. Thus, electrical driving can overcome conventional microwave coupling, showing that it can be used to efficiently drive singlet-triplet spin transitions in graphene nanostructures.

In order to assess the strength of the system response to the electrically driven spin resonance, it is important to compare the Rabi coupling, that drives the TLS out of equilibrium, with the spin relaxation $T_1$ and decoherence $T_2$ times. For instance, the steady state solution of the Bloch equation for a TLS driven with a resonant ac Rabi coupling is fully determined by the dimensionless constant $x = \Omega^2 T_1 T_2$ (see supplementary material). Both $T_1$ and $T_2$ depend a lot on whether the nanographenes are deposited on top of a conductor or an insulator. In the former case, exchange interaction with the electrons in the conductor will be the dominant spin relaxation and decoherence mechanism \[ \text{[23]}. \]

We now provide a rough estimate of the contribution to $T_2$ coming from an intrinsic mechanism, namely, the hyperfine coupling with the nuclear spins of the hydrogen atoms that passivate the carbon atoms. Given that the natural abundance of spinless $^{12}$C is 99 percent, hyperfine interaction with carbon is less important. In addition, isotopically pure graphene could be used and get rid of $^{13}$C completely. In principle, hyperfine interaction between the graphene unpaired electronic spins and the edge hydrogens has two components, the contact Fermi interaction and the dipole-dipole interaction. The former is stronger, in general, and depends on the probability for the electrons in the zero mode states to visit the hydrogen 1s orbital. It can be seen right away that hybridization of the $p_z$ orbitals of carbon with the 1s orbital of hydrogen is zero when these atoms lie in the same plane. Therefore, Fermi contact interaction with edge hydrogen atoms vanishes altogether and we are left with the dipolar coupling.

The electronic spins will undergo dephasing due to the stochastic addition of the magnetic field created by the nuclear magnetic moments. In order to estimate this effect, we treat the nuclear moments as classical independent random variables $\vec{n}_N$. The average nuclear magnetic field is zero, but the standard deviation $\vec{B}_z$ is not. We assume that the nuclear spins undergo a stochastic motion with a white noise spectrum with correlation time $\tau$. Under these assumptions, the $T_2$ dephasing time for the electronic transitions due to their hyperfine interaction with the edge hydrogen atoms is \[ T_2^{-1} = \left( \frac{g_\mu_B B_{ac}}{\hbar} \right)^2 \tau. \] This equation is valid as long as $\tau$ is the shortest time-scale in the problem \[ \text{[24,25]}. \] In particular, $\tau < \omega_0^{-1}$, where $\omega_0$ is the electronic Zeeman splitting. Therefore, in its range of validity, the upper limit for the decoherence rate is given by $T_2^{-1} < \left( \frac{g_\mu_B B_{ac}}{\hbar} \right)^2 \frac{2}{\Omega}$. In the suppl. mat. we have obtained $B_z \approx 1 \text{mT}$. This small field produces a electronic Zeeman splitting of 120
neV. The resulting estimate for the decoherence rate is $T_2 > 0.5\text{ms}$. Using $T_1 > T_2$ we can obtain a lower limit for $x = \Omega^2 T_1 T_2 > \Omega^2 T_2$. For $\hbar \Omega = 1 \text{meV}$, we obtain $x >> 100$. So, the intrinsic decoherence mechanism does not pose an obstacle for the proposed electric manipulation of the spin states of singlet-triplet states in graphene nanostructures.

Discussion and Conclusions.
We have identified a class of graphene nanostructures that host local spin moments in the form of pairs of antiferromagnetically coupled electrons. We have presented a full quantum theory for these local moments that goes beyond the broken symmetry mean-field and DFT based calculations. We have identified a new mechanism to efficiently drive spin transitions by application of an off-plane electric field. The mechanism, particularly efficient in graphene nanostructures, relies on the electrically driven breakdown of mirror symmetry that generates of spin-orbit coupling in the single-particle wave functions. In turn, this induces and antisymmetric Dzyaloshinsky-Moriya exchange in the spin Hamiltonian that mixes the $S = 0$ ground state with the $S_z = \pm 1$ states of the triplet. The strength of the Rabi coupling is found to exceed the one obtained for $S = 1/2$ with state of the art conventional spin resonance driven with microwaves. Importantly, the proposed mechanism permits to drive transitions that are forbidden in conventional spin resonance experiments.

The proposed mechanism is different from other proposals for electrically driven spin resonance. Some of them rely on the modulation of the crystal field Hamiltonian. Others, on the slanting magnetic or exchange field of a nearby magnetic electrode. Our findings could be used to manipulate individual pairs of spins in nanographene structures. The independent progress in spin resonance driven by scanning tunneling microscopes and in the fabrication of atomically defined graphene nanostructures with bottom-up techniques could permit to explore their potential for spin qubits.

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Appendix A: Mean field Hubbard model

The exact solution for the Hubbard model is only possible in some very specific instances, such as a 1d chain, by means of Bethe ansatz, or in small clusters via numerical diagonalization. For the nanographenes considered here, we make use of the so called mean field approximation, where the exact 4-fermion operator is replaced by

$$V_{MF} = U \sum_i (n_{i\uparrow} n_{i\downarrow} + n_{i\downarrow} n_{i\uparrow} - \langle n_{i\uparrow}\rangle \langle n_{i\downarrow}\rangle) \tag{A1}$$

where $\langle n_{i\alpha}\rangle$ stands for the average number operator, evaluated with the eigenstates of the mean field Hamiltonian obtained from the sum of $V_{MF}$ and the single-particle part. Of course, this defines a self-consistent problem, that is solved by numerical iteration. Depending on the atomic structure of the nanographene, and the ratio $U/t$, the mean field self-consistent solutions can describe broken symmetry solutions with local moments, or non-magnetic solutions.

Appendix B: Exact solution of 2 site Hubbard model

The Hilbert space for the 2 site Hubbard model with 2 electrons (half filling) has a dimension of 6, spanned by the basis set of Fock states in the site representation $(2, 0)$, $(0, 2)$, $(\uparrow, \uparrow)$, $(\downarrow, \downarrow)$, $(\downarrow, \uparrow)$ and $(\uparrow, \downarrow)$ with a self-evident notation, so that the first (second) state represents a doubly occupied $A$ ($B$) site, the third state denotes the two sites with single occupation with a $S_z = +1/2$ each, and so on. In this basis set, the Hamiltonian matrix is readily calculated, taking into account the sign that arises from the definition of the Fock states in terms of the second quantization operator, as:

$$H = \begin{pmatrix} \hat{U} & 0 & -\hat{t}_R & -\hat{t}_R & -\hat{t} & \hat{t} \\ 0 & \hat{U} & -\hat{t}_R & -\hat{t}_R & -\hat{t} & \hat{t} \\ -\hat{t}_R & -\hat{t}_R & g_{\mu B} B_z & 0 & 0 & 0 \\ -\hat{t}_R & -\hat{t}_R & 0 & -g_{\mu B} B_z & 0 & 0 \\ -\hat{t} & -\hat{t} & 0 & 0 & 0 & 0 \\ \hat{t} & \hat{t} & 0 & 0 & 0 & 0 \end{pmatrix} \tag{B1}$$

For $t_R$ and $B_z = 0$, and in the relevant limit with $\hat{t} \ll \hat{U}$, the eigenvalues are, in increasing order of energy, a singlet, a triplet, and two more non-degenerate singlets (see Figure 1(a)). We define the weight of the $(2, 0)$ and $(0, 2)$ configurations on the ground state singlet, $P_2 = |\langle 20 | \Psi_G \rangle|^2 + |\langle 02 | \Psi_G \rangle|^2$. The smaller $P_2$, the better the approximation of the spin model to describe the singlet and triplet states. The dependence of $P_2$ on $W$ and $U/t$ is shown in figure for rectangular graphene nanoribbons. It is apparent that, except for very small for $U = t$ and $W > 10$, $P_2$ is below 0.05. It is also apparent that there is a smooth crossover from the non-interacting limit, for which $P_2 = 0.5$, and the local moment limit for which charge fluctuations are frozen.

Appendix C: Electronic dipolar interaction

Here we consider the effect of the dipole-dipole coupling between the magnetization cloud of state $\psi_A$ with
state $\psi_B$. This leads to an additional term in the spin Hamiltonian:

$$H_{\text{dip}} = \sum_{a,b} D_{ab} S_a(1) S_b(2) \quad (C1)$$

where $a = x, y, z$ and

$$D_{ab} = (g\mu_B)^2 \frac{\mu_0}{4\pi} \Lambda_{ab} \quad (C2)$$

where

$$\Lambda_{ab} = \sum_{i,i'}|\psi_L(i)|^2 |\psi_R(i')|^2 \frac{\delta_{a,b} - 3n_a(i) n_b(i')}{r_{ii'}^3} \quad (C3)$$

Our numerical calculations confirm that only the diagonal terms of the tensor are finite, as expected from symmetry. We show them in figure 6 for rectangular graphene nanoribbons. The elongated shape of ribbons, accounts for the difference between $D_{xx}$ and $D_{yy}$. The resulting dipolar interaction can be written as:

$$H_{\text{dip}} = -D_{xx} S_x(1) S_x(2) + D_{zz} S_z(1) S_z(2) \quad (C5)$$

Importantly, this Hamiltonian does not couple states with different total $S_z$. Therefore, the dipolar interaction does not couple the two states in the two level system formed by the $S = 0$ ground state with the $S_z = -1$ state (equation 14). The only effect of the dipolar interaction is to introduce a small anisotropy splitting in the triplet manifold.

FIG. 6: Dipolar interaction, as defined in equation (C2), for rectangular graphene nanoribbons, as a function of ribbon size $W$.

Appendix D: Hyperfine interaction

The hyperfine interaction is the sum of two dominant contributions, Fermi contact interaction and dipolar coupling. The first is given by the overlap of the electronic quantum state with the nuclear species in question. The Fermi-contact contribution to the hyperfine interaction of the edge electron, $A$ or $B$, on a given hydrogen atom, denoted with the label $N$, is computed by calculating the weight of the wave function on the $s$ orbital of that atom and multiplying the weight to the hyperfine interaction of atomic hydrogen, 1024 MHz. In order to estimate the contact interaction we adopt a tight-binding model that permits to compute how the $\pi$ orbitals of graphene hybridize with the $s$ orbital of hydrogen. This can be done using the TB model with 4 orbitals per carbon atom, and one orbital per hydrogen atom. Within this model, the mid-gap states are, in principle, a linear combination of $p_z$, $p_x$, $p_y$ and $s$ orbitals of the carbon atoms and the $s$ orbital of the edge hydrogen atoms. However, for flat structures with mirror symmetry, the $p_z$ orbitals are odd under reflection, and are thereby perfectly decoupled from all the other states of the basis set, that are even. As a result, within this model we find that the Fermi contact contribution to the hyperfine interaction vanishes for the mid-gap states, as well as all the low energy states, as long as the edge hydrogen atoms remain in the same plane than the nanographene, which is their equilibrium position.

We thus are left with hyperfine dipolar coupling, whose magnitude we estimate here. Since we are interested in the decoherence induced by the nuclear spins on the elec-
tronic states, we treat the nuclear spins as classical magnetic moments $\vec{m}_N$, whose orientation is completely random. At any given time they create a magnetic field at a carbon site $\vec{r}_i$

$$\vec{B}_i[\vec{m}_N] = \frac{\mu_0}{4\pi} \sum_N \frac{\vec{m}_N - 3\vec{n}_{N_1} \cdot \vec{m}_N}{|\vec{r}_N - \vec{r}_i|^3}$$ (D1)

where the index $N$ runs over the edge hydrogen atoms and $\vec{n}_{N_1}$ is the unit vector along the direction that joins the nuclear spin $N$ and the carbon site $i$. We now write down the electronic magnetization density as:

$$\vec{m}_e(i) = \frac{1}{2} \vec{r}_{\sigma,\sigma'} \left( |\psi_A(i)|^2 a_{\sigma}^\dagger a_{\sigma'} + |\psi_B(i)|^2 b_{\sigma}^\dagger b_{\sigma'} \right)$$ (D2)

where $\vec{r}_{\sigma,\sigma'}$ are the spin 1/2 Pauli matrices with eigenvalues ±1.

It is now convenient to define the average nuclear magnetic field by the electronic states:

$$\vec{B}_{A,B} = \sum_i |\psi_{A,B}(i)|^2 \vec{B}_i[\vec{m}_N]$$ (D3)

This permits to write the interaction of the electronic spins in states $A$ and $B$ with the nuclear spins as:

$$V_N = -\sum_i \vec{m}_e(i) \cdot \vec{B}_i[\vec{m}_N]$$ (D4)

where

$$\vec{S}_{\sigma,\sigma'}^A = \frac{1}{2} \vec{r}_{\sigma,\sigma'} a_{\sigma}^\dagger a_{\sigma'} \quad \vec{S}_{\sigma,\sigma'}^B = \frac{1}{2} \vec{r}_{\sigma,\sigma'} b_{\sigma}^\dagger b_{\sigma'}$$ (D5)

In the strong coupling limit $\hat{U} \gg \hat{\tau}$ this results in the addition of the stochastic magnetic field to the Zeeman contribution in equation (10).

The nuclear field component along the $z$ direction modifies the energy of the $S_z = 1$ state of the TLS, and leaves the energy of the $S = 0$ unchanged. Therefore, it induces a shift of the TLS splitting, defined by equation (14), by an amount

$$\delta\omega_0 = \frac{g\mu_B}{\hbar} (\vec{B}_{z,A} + \vec{B}_{z,B})$$ (D6)

which is a functional of the nuclear magnetic moments. For nanoribbons and heterojunctions, the mirror symmetry of the structures gives $\vec{B}_{z,A} = \vec{B}_{z,B} \equiv \vec{B}_{z,B}$.

We take the orientation of the nuclear moments as random variables with an uniform distribution, given that even at mK temperatures, nuclear Zeeman splitting is much smaller than $k_BT$:

$$\langle \vec{m}_N \rangle = 0 \quad \langle m_{N,1} m_{N,i}^\dagger \rangle = \delta_{a,a'} \delta_{N,N'} \frac{m_0^2}{3}$$ (D7)

where $m_0$ is the proton magnetic moment.

As a result, its straightforward to see that the average over nuclear moment realizations vanishes, $\langle \vec{B}_{A,B} \rangle = 0$. The standard deviation of the components, defined as:

$$\vec{B}_{a,A,B}^2 = \frac{\mu_0^2 m_0^2}{(4\pi)^2} \sum_{i,i',N} |\psi_A(i)|^2 |\psi_A(i')|^2 \eta(N, i, i')$$ (D8)

where

$$\eta(N, i, i') = 1 + n_i n_i' + 3(n_i n_i' - 3(n_i^2 + n_i'^2))^2$$ (D9)

In the case of the $a = z$ component we have $n^2 = 0$ for all $N$ and $i$. We can obtain a quick estimate for the edge states in the graphene nanoribbons if we approximate the wave function as equally distributed in 5 edge carbon atoms and only consider their coupling to the first neighbor hydrogen. In that case, we have:

$$\vec{B}_z^2 \simeq \frac{\mu_0^2 m_0^2}{(4\pi)^2} \frac{1}{3} \frac{1}{d_{HC}^2} \equiv \frac{1}{3} (b_0)^2$$ (D10)

where $d_{HC} \simeq 1.1\AA$ is the carbon-hydrogen bond length and $b_0 \simeq 1mT$ is the magnitude of the magnetic field created by a proton at a distance $d_{HC}$. From this, we can estimate the associated shift $\hbar \delta\omega_0 \simeq 120\text{neV}$. Our numerical calculation of (D9) yields $\vec{B}_z = 0.2\text{ mT}$ for a nanoribbon with $W = 10$, in line with the estimate of equation (D11).

### Appendix E: Steady State solution of driven two level system

The steady state solution of the Bloch equation for a two level system driven by an a.c. Rabi monochromatic signal with frequency $\omega$ is given by:

$$P_0 - P_1 = \delta P_{eq} \left( 1 - \frac{\Omega^2 T_1 T_2}{1 + (\omega - \omega_0)^2 T_2^2 + \Omega^2 T_1 T_2} \right)$$ (E1)

where $P_0$ and $P_1$ are the non-equilibrium occupation of the ground and excited states in equation (14) and $\delta P_{eq} \equiv \tanh \left( \frac{\hbar \omega_0}{2k_BT} \right)$ is the equilibrium population imbalance. Thus, a relevant figure to assess the merit of the electrical control of the spin on electrically driven graphene nanostructures is $x^2 = \Omega^2 T_1 T_2$. In resonance, we have $P_0 - P_1 = \delta P_{eq} \frac{1}{1+x^2}$. Thus, the maximal departure from equilibrium is obtained for very large $x$. 


In the work of Min et al, the effective Hamiltonian at the Dirac point is derived, and the Rashba coupling, denoted by $\lambda_R$ is used. When that effective Hamiltonian at the Dirac point is derived from the tight-binding expression (equation 8), it is found that $\lambda = -3t_R$. From equation 8 we can derive the effective Hamiltonian at the Dirac points of 2D graphene.