Adiabatically twisting a magnetic molecule to generate pure spin currents in graphene

Firoz Islam and Colin Benjamin

National institute of Science education and Research, Bhubaneswar 751005, India

E-mail: cbiop@yahoo.com

Received 30 September 2015, revised 4 December 2015
Accepted for publication 7 December 2015
Published 6 January 2016

Abstract
The spin–orbit effect in graphene is too muted to have any observable significance with respect to its application in spintronics. However, graphene technology is too valuable to be rendered impotent to spin transport. In this communication we look at the effect of adiabatically twisting a single-molecule magnet embedded in a graphene monolayer. Surprisingly, we see that pure spin currents (zero charge current) can be generated from the system via quantum pumping. In addition we also see that spin-selective current can be pumped from the system. The pure spin current seen is quite resilient to temperature while disorder has a limited effect. Furthermore, the direction of these spin-pumped currents can be easily and exclusively controlled by the magnetization of the single-molecule magnet, with disorder having no effect on the magnetization control of the pumped spin currents.

Keywords: quantum pumping, spintronics, single-molecule magnet, graphene, disorder

(Some figures may appear in colour only in the online journal)

I. Introduction
Graphene has been a revolutionary material of the 21st century. It is remarkable that since its discovery around a decade ago it has captured the interest of the scientific community in ways that even high-$T_c$ superconductors in their heyday could not. A cursory look at graphene’s properties would provide reasons for this. Graphene is light with huge tensile strength and crucially, in contrast to most materials, electronic energy is linearly proportional to its wave vector and not to its square; also it shows quite remarkable quantum phenomena such as Klein tunneling [1] and a room-temperature quantum Hall effect [2], etc. Notwithstanding the many advantages of using graphene to transport electrons faster and with less dissipation, it has been observed that the spin–orbit effect in graphene is at best negligible, thus making these advantages of no practical use for applications in spintronics. So how do we exploit the manifest advantages of graphene and marry them to spintronics? In this communication we address this issue. We intend to embed a monolayer of graphene with a single-molecule magnet (SMM). We then adiabatically modulate two independent parameters of the resulting system to pump a pure spin current. One of these parameters is the magnetization strength of the magnetic molecule, which has been shown to be controlled by twisting it [3]. Secondly, we add a delta function-like point interaction, which can be either an isolated adatom in the graphene monolayer or an extended line defect, or even a very thin potential barrier whose strength is controlled by a gate voltage. Using these two parameters we intend to pump a pure spin current.

Adiabatic quantum pumping is a means of transferring charge and/or spin carriers by the cyclic variation of two independent system parameters without applying any external perturbation (such as voltage bias, etc). The theory of adiabatic quantum pumping was developed in 1998 [4] based on the fact that adiabatic modulations of a two-dimensional electron gas (2DEG) can lead to changes in the local density of states and thus current transport. In 1999, an adiabatic quantum electron pump was reported in an open quantum dot where the pumping signal was produced in response to the cyclic deformation of the confining potential [5]. The variation of the dot’s shape changes electronic quasi-energy states of the dot, thus ‘pumping’ electrons from one reservoir to another.

The AC voltages applied to the quantum dot in order to change its shape result in a DC current when the reservoirs are in equilibrium. This non-zero current is produced only if
there are at least two time-varying parameters in the system because a single-parameter quantum pump does not transfer any charge. The study of the adiabatic pumping phenomenon was later extended to adiabatic spin pumping in both experiment and theory [6, 7]. In the experiment on quantum spin pumping one generates a pure spin current via a quantum dot by applying an in-plane magnetic field that is adiabatically modulated to facilitate a net transfer of spin. Many spintronic devices, such as the spin valve and magnetic tunneling junctions [8], are associated with the flow of spin-polarized charge currents. Spin-polarized currents coexist with charge currents and are generated when an imbalance between spin-up and spin-down carriers is created, for example by using magnetic materials or applying a strong magnetic field or by exploiting spin–orbit coupling in semiconductors [8]. Spin transport aided by a bias voltage has been studied previously [9–11].

More recently, there has been increasing interest in the generation of pure spin current by quantum pumping without an accompanying charge current [6]. In monolayer graphene, a group has attempted to address this issue by proposing a device consisting of ferromagnetic strips and gate electrodes [12]. However, ferromagnetic strips in graphene are unwieldy and lead to further complication as spin polarization is lost at the ferromagnet–graphene interface. In this work we look at just a piece of monolayer graphene without any ferromagnets but with two impurities—one magnetic (the SMM) and the other non-magnetic. By independently modulating these two we show the generation of pure spin currents. The generation of a pure spin current is possible only if all spin-up electrons flow in one direction and an equal number of spin-down electrons flow in the opposite direction. In this case the net charge current \( I_{\text{charge}} = I_I + I_{\bar{I}} \) vanishes while a finite spin current \( I_{\text{spin}} = I_I - I_{\bar{I}} \) exists, because \( I_I = -I_{\bar{I}} \), where \( I_I \) and \( I_{\bar{I}} \) are the electron currents with spin up and spin down. Furthermore, we also see the generation of spin-selective currents, namely either only \( I_I \) or \( I_{\bar{I}} \), and this implies that the total magnitude of the charge current is identical to that of the spin current.

In this work we show how pure spin currents and spin-selective currents can be generated by twisting a single-molecule magnet. Single-molecule magnets are of great importance for molecular spintronics. Such molecules can now be synthesized, for example the molecule Mn12·ac, which has a ground state with a large spin \( S = 10 \), and a very slow relaxation of magnetization at low temperatures [13]. SMMs do not just have integer spin values; a number of SMMs like the complex Mn4O3 [14] have large half-integer spin \( S = 9/2 \). However, in a literal twist to this tale (pun intended), a few years back scientists revealed that these big spin molecules can be twisted and thus their magnetization can be easily altered [15]. This fact we utilize in our adiabatic pumping mechanism. The mechanism of twisting is not difficult to implement. SMMs have a metallic core (for example in Mn12 complexes the metallic core consists of the Mn–O–N–Mn moiety), and a deliberate targeted structural distortion of it leads to such a large change in the magnetization of the SMM that an initially ferromagnetic SMM can undergo a twist to an antiferromagnetic SMM. The twist can be effectively controlled by two methods: (i) a simple substitution of one type of atom (in Mn12 complexes a H atom) by another sterically demanding atom (again in Mn12 complexes by a Me, Et, Ph, etc atom) or (ii) the use of hydrostatic pressure [16]. In the latter method external hydrostatic pressure is applied on the SMM, leading to a twisting of the metallic core and thus a net change in magnetization. Therefore, the pressure method is much more amenable to the quantum pumping mechanism wherein the pressure applied could be continuously changed, albeit adiabatically, leading to an adiabatic change in magnetization and thus to the exchange interaction \( J \).

II. Theory

Graphene is a monatomic layer of graphite with a honeycomb lattice structure [18] that can be split into two triangular sublattices A and B. The electronic properties of graphene are effectively described by the massless Dirac equation. The presence of isolated Fermi points, \( K \) and \( K' \), in its spectrum gives rise to two distinctive valleys. We consider a sheet of graphene on the \( x-y \) plane. In figure 1 we sketch our proposed system. For a quantitative analysis we describe our system by the massless Dirac equation in the presence of an embedded SMM. The Hamiltonian used to describe a SMM has the following terms:

\[
H_{\text{SMM}} = -DS_z^2 - Js \cdot S. \tag{1}
\]

The first term represents the energy of the SMM. \( D \) is a uniaxial anisotropy constant and \( S_z \) is the z-component of the spin of the molecular magnet. The second term is most relevant to us since we deal with electron transport. The Dirac electrons in graphene interact with the SMM only via the exchange term \(-Js \cdot S\). Furthermore, the magnitude of \( D \) in a realistic SMM is very small compared to \( J, D = 0.292 K = 0.025 \text{ meV} \) while \( J = 100 \text{ meV} \), almost a few thousand times larger [17]. Though anisotropy is very important in preserving the intrinsic
properties of the SMM, its effect on conduction electrons is barely a small correction to the energy, nothing more. The first term will only be relevant in electronic structure calculations; it is not relevant for electronic transport calculations and the only term of interest is the exchange coupling. Thus we consider only the second term in the subsequent analysis. We consider a single-molecule magnet at \( x = 0 \) and another electrostatic delta potential at \( x = a \). The Hamiltonian of a Dirac electron moving in the \( x \)-direction can be written as

\[
H = h v F \cdot p + J_s \cdot S \delta(x) + V \delta(x - a). \tag{2}
\]

The first term represents the kinetic energy term for graphene with \( \sigma \) the Pauli matrices that operate on the sublattices A and B, and \( p = (p_x, p_y) \) the 2D momenta; the second term is for an electron interacting with the SMM and the third term is an electrostatic delta potential. In the second term \( J \) represents the exchange interaction, which depends on the magnetization of the SMM; twisting the SMM changes the magnetization, thus effectively changing \( J \). \( s \) represents the spin of the Dirac electron while \( S \) represents the spin of the SMM. \( V \) represents strength of the adatom situated at a distance \( a \) from the SMM. Here \( h \) and \( v_F \) are Planck’s constant and the energy-independent Fermi velocity for graphene.

Equation (2) is valid near the valley \( K \) in the Brillouin zone and \( \Psi = [\psi_K^{1}(r), \psi_K^{2}(r)] \) is a spinor containing the electron fields in each sublattice. The Hamiltonian for the valley \( K \) can be obtained by replacing \( p_x \) by \( -p_x \) in equation (2). Because of this symmetry, \( H_K(p_x) = H_K(-p_x) \), transport coefficients will be the same in both valleys. So we confine our discussion to the valley \( K \).

To calculate the quantum spin-pumped currents we need to introduce the basic theory of quantum pumping, which is quite well known, as well as solve the scattering problem for an electron with spin (up or down) incident from either left or right. We introduce them below.

II.A. Quantum pumping current

To calculate the quantum pumping current we proceed as follows. The charge passing through a lead \( \mu \) to the left of the molecular magnet, due to an infinitesimal change in system parameters, is given by

\[
dQ_{\sigma \nu}(t) = e \left[ \frac{dN_{\mu \nu}}{dX_1} \delta X_1(t) + \frac{dN_{\mu \nu}}{dX_2} \delta X_2(t) \right]. \tag{3}
\]

with the spin current transported in one period being

\[
I_{\sigma \nu} = \frac{e w}{2\pi} \int_0^{\tau} dt \left( \frac{dN_{\mu \nu}}{dX_1} \frac{dX_1}{dt} + \frac{dN_{\mu \nu}}{dX_2} \frac{dX_2}{dt} \right). \tag{4}
\]

In the above \( \tau = 2\pi/v_F \) is the cyclic period. The quantity \( dN_{\sigma \nu}/dX_1 \) is the emissivity, which is determined from the elements of the scattering matrix in the zero-temperature limit by

\[
\frac{dN_{\mu \nu}}{dX_1} = \frac{1}{2\pi} \sum_{\sigma'\nu'} \text{Im} \left[ \frac{\partial (s_{\sigma\nu}^{\sigma'})}{\partial X_1} \frac{s_{\mu\nu}^{\sigma'}}{s_{\mu\nu}^{\sigma'}} \right]. \tag{5}
\]

Here \( s_{\sigma\nu}^{\sigma'} \) denote the elements of the scattering matrix as denoted above; it is evident that \( \mu, \nu \) and \( i \) can only take values 1 and 2, while \( \sigma \) and \( \sigma' \) take values \( \uparrow \) and \( \downarrow \) depending on whether spin is up or down. The symbol \( \text{Im} \) represents the imaginary part of the complex quantity inside parenthesis.

The spin pump we consider is operated by adiabatically twisting the magnetic molecule, thus modulating the magnetic interaction between the magnetic molecule and scattered electrons, \( J \), and the strength of the ‘delta’ function potential \( V \); here \( X_1 = J = J_0 + J_p \sin(\omega t) \) and \( X_2 = V = V_0 + V_p \sin(\omega t + \theta) \). A paragraph on the experimental feasibility of the proposed device is given above the conclusion. As the pumped current is directly proportional to \( \omega \) (the pumping frequency), we can set it to be equal to 1 without any loss of generality.

By using Stokes’ theorem on a two-dimensional plane, one can change the line integral of equation (4) into an area integral (see [6] for details):

\[
I_{\sigma \nu} = e \int_A \frac{dX_1 dX_2}{2\pi} \sum_{\sigma'\nu'} \left( \frac{\partial s_{\sigma\nu}^{\sigma'}}{\partial X_1} \frac{\partial s_{\nu\sigma'}^{\sigma'}}{\partial X_2} - \frac{\partial s_{\sigma\nu}^{\sigma'}}{\partial X_2} \frac{\partial s_{\nu\sigma'}^{\sigma'}}{\partial X_1} \right). \tag{6}
\]

Substitution of equation (5) into equation (6) leads to

\[
I_{\sigma \nu}(\theta) = e w \delta \delta \frac{\sin(\theta)}{2\pi} \sum_{\nu'\nu} \left( \frac{\partial s_{\nu\sigma'}^{\sigma'}}{\partial X_1} \frac{\partial s_{\nu'\sigma'}^{\sigma'}}{\partial X_2} \right). \tag{7}
\]

This current is for a particular angle of incidence (\( \theta \)) because the scattering amplitudes depend on \( \theta \). So hereafter, we replace \( I_{\sigma \nu} \) by \( I_{\nu}(\theta) \). If the amplitude of oscillation is small, i.e. for sufficiently weak pumping (\( \delta X_1 < X_0 \)), we have

\[
I_{\nu}(\theta) = \frac{e w \delta \delta}{2\pi} \sin(\theta) \sum_{\nu'\nu} \left( \frac{\partial s_{\nu\sigma'}^{\sigma'}}{\partial V} \frac{\partial s_{\nu'\sigma'}^{\sigma'}}{\partial V} \right). \tag{8}
\]

In the considered case of a magnetic molecule and delta function potential the case of very weak pumping is defined by \( \delta X_1 \ll X_0 \), and equation (8) becomes

\[
I_{\nu}(\theta) = I_0 \sum_{\nu'\nu} \left( \frac{\partial s_{\nu\sigma'}^{\sigma'}}{\partial V} \frac{\partial s_{\nu'\sigma'}^{\sigma'}}{\partial V} \right), \tag{9}
\]

wherein

\[
I_0 = \frac{e w \delta \delta}{2\pi} \sin(\theta). \tag{10}
\]

We are considering pumped currents into only lead 1 (to the left of the magnetic molecule), therefore \( \nu = 1 \). Further, we drop the index \( \nu \) in expressions below.

For weak pumping, we have the total pumped spin-up current given as

\[
I_{\uparrow}(\theta) = I_0 \left[ \left( \frac{\partial s_{\uparrow\uparrow}^{\uparrow\uparrow}}{\partial V} \frac{\partial s_{\uparrow\uparrow}^{\uparrow\uparrow}}{\partial V} \right) + \left( \frac{\partial s_{\uparrow\downarrow}^{\uparrow\downarrow}}{\partial V} \frac{\partial s_{\downarrow\uparrow}^{\uparrow\downarrow}}{\partial V} \frac{\partial s_{\uparrow\downarrow}^{\uparrow\downarrow}}{\partial V} \frac{\partial s_{\downarrow\uparrow}^{\uparrow\downarrow}}{\partial V} \right) + \left( \frac{\partial s_{\uparrow\downarrow}^{\uparrow\downarrow}}{\partial V} \frac{\partial s_{\downarrow\uparrow}^{\uparrow\downarrow}}{\partial V} \right) \right]. \tag{11}
\]
Similarly, we can calculate the spin-down current for the case of weak pumping by replacing $\uparrow$ by $\downarrow$ and vice versa.

For strong pumping, we have the total spin-up current given as

$$I_i = \frac{e\omega}{2\pi} \int_0^\pi dr \left[ \frac{dN_{\uparrow}}{d\xi_1} d\xi_1 + \frac{dN_{\downarrow}}{d\xi_2} d\xi_2 \right],$$

with

$$\frac{dN_{\uparrow}}{d\xi_1} = \frac{1}{2\pi} \left\{ \frac{\partial s_{11}^{\uparrow}}{\partial \xi_1} s_{11}^{\uparrow \uparrow} + \frac{\partial s_{12}^{\uparrow}}{\partial \xi_1} s_{12}^{\uparrow \downarrow} \right\},$$

$$\frac{dN_{\downarrow}}{d\xi_2} = \frac{1}{2\pi} \left\{ \frac{\partial s_{12}^{\downarrow}}{\partial \xi_2} s_{12}^{\downarrow \uparrow} + \frac{\partial s_{11}^{\downarrow}}{\partial \xi_2} s_{11}^{\downarrow \downarrow} \right\} \right\}.$$  \hspace{1cm} (11)

where we have dropped the lead index since we pump always to the left lead (left to SMM) and $s_{\mu\nu}^{\sigma\sigma'}$ is the complex conjugate of $s_{\mu\nu}^{\sigma\sigma'}$. To obtain the total current, we integrate over $\phi$. Then the total spin-up pumped current for both weak and strong pumping becomes

$$I_i = \int_{-\pi/2}^{\pi/2} I_i(\phi) \cos(\phi) d\phi.$$  \hspace{1cm} (12)

Similarly, we can calculate the spin-down current for the case of weak pumping by replacing $\uparrow$ by $\downarrow$ and vice versa. In the above equations the scattering amplitudes represent:

- $s_{11}^{\uparrow}$, the reflection amplitude when a spin-up electron is coming from the left side and is reflected into the spin-up state.
- $s_{11}^{\downarrow}$, the reflection amplitude when a spin-down electron is coming from the left side and is reflected into the spin-up state.
- $s_{12}^{\uparrow}$, the transmission amplitude when a spin-up electron is coming from the right side and is transmitted into the spin-up state.
- $s_{12}^{\downarrow}$, the transmission amplitude when a spin-down electron is coming from the right side and is transmitted into the spin-up state.

Numerically, we have calculated $r_i$, $r_i'$, $t_i$, and $t_i'$ and substituted them in the above expression to obtain the spin-up pumping current.

**Effect of finite temperature.** So far our discussion is for zero temperature. The effects of temperature could be easily captured by multiplying the pumping current by a factor $-df(E)/dE$ and integrating over the energy of the incident electron [19], i.e.

$$I_\sigma = \int_{-\pi/2}^{\pi/2} \int_0^\infty \left( -\frac{df(E)}{dE} \right) I_\sigma(\phi) \cos(\phi) dE \ d\phi, \quad \sigma = \uparrow, \downarrow.$$  \hspace{1cm} (13)

where $f(E)$ is the Fermi–Dirac distribution function.

**II.B. Solving the scattering problem**

Let us consider an incident spin-up electron from the left of the magnetic molecule ($x < 0$) with energy $E$. The electron can be reflected or transmitted into a spin-up/down state. Then the spinors, for the angle of incidence $\phi$, in the various regions are given as follows.

**Region I** ($x < 0$):

$$\psi_I(\phi) = \left[ (e^{ikx} + r_{1e} e^{-ikx}) \chi_m \right] r_{2e} e^{-ikx} \chi_{m+1},$$

$$\psi_{II}(\phi) = \left[ (e^{ikx} + r_{1e} e^{-ikx}) \chi_m \right] -r_{2e} e^{-ikx} \chi_{m+1}.$$  \hspace{1cm} (14)

**Region II** ($0 < x < a$):

$$\psi_{III}(\phi) = \left[ a_1 e^{ikx} + b_1 e^{-ikx} \right] \chi_m,$$

$$\psi_{IV}(\phi) = \left[ a_1 e^{ikx} + b_1 e^{-ikx} \right] \chi_m.$$  \hspace{1cm} (15)

**Region III** ($x > a$):

$$\psi_{V}(\phi) = \left[ t_{2e} e^{ikx} \chi_m \right] t_{1e} e^{ikx} \chi_{m+1},$$

$$\psi_{VI}(\phi) = \left[ t_{2e} e^{ikx} \chi_m \right] t_{1e} e^{ikx} \chi_{m+1}.$$  \hspace{1cm} (16)

In the above equations, $\uparrow$ and $\downarrow$ stand for spin-up and spin-down electrons. Here, $r_i, r_i', t_i,$ and $t_i'$ are the reflection and transmission amplitudes respectively. Also, $k = E_k \cos(\phi)$ with $E_k (> 0)$ being the Fermi energy. $\chi$'s denote the eigenstates of $S_k$, the $z$-component of the spin operator for the SMM; $S_k \chi_m = m \chi_m$ with $m$ being the corresponding eigenvalue. The scattering is elastic and the exchange interaction conserves the $z$-component of the total spin $S + s$. The exchange operator in the Hamiltonian, $s \cdot S = s_x S_x + (1/2) s_y (S^+ S^- + S^- S^+)$, acts as a spin-flipper for electrons with different values of $s_x$ to those of $S_x$, while for the same values it acts as a normal barrier, $s \cdot S = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$, $\chi_m = F \begin{pmatrix} 1 \\ 0 \end{pmatrix} \chi_m$ with $F = \sqrt{(S-m)(S+m+1)}$ and $S^+ = S + iS_y$ and $S^- = S - iS_y$ are the raising and lowering operators.

In solving the scattering problem from a delta potential the following two boundary conditions have to be met: (i) continuity of the wavefunctions at the boundary and (ii) discontinuity of the energy at the boundary. However, these boundary conditions work only if the system is described by the Schrödinger equation, and not for a Dirac material like graphene. For the Dirac equation, the wavefunctions on either side of the delta potential are not continuous across the boundary.

At $x = 0$, while taking integration on the both sides of the Dirac equations, $H \psi = E \psi$, one is stuck at the following integration:
where the delta function potential mentioned is not an exact one but a point-like interaction [20, 21]. The above idea can be deployed at the boundary $x = 0$, which leads to the two equations as

$$-i\hbar v_F [\psi_B^I(x = 0^+) - \psi_B^I(x = 0^-)] = \frac{\hbar}{2} \gamma \cdot \mathbf{S}[\psi_B^I(x = 0^+) + \psi_B^I(x = 0^-)].$$

(22)

and

$$-i\hbar v_F [\psi_A^I(x = 0^+) - \psi_A^I(x = 0^-)] = \frac{\hbar}{2} \gamma \cdot \mathbf{S}[\psi_A^I(x = 0^+) + \psi_A^I(x = 0^-)].$$

(23)

After substituting the wavefunctions in equations (22) and (23),

$$a_1(i\alpha c + e^{-i\phi}) + a_2(i\alpha F) + b_1(i\alpha c - e^{-i\phi}) + b_2(i\alpha F) + r_1(i\alpha c + e^{-i\phi}) + r_2(i\alpha F) = e^{i\phi} - i\alpha c,$$

(24)

$$a_1(i\alpha F) + a_2[e^{i\phi} - i\alpha(m + 1)] + b_1(i\alpha c - e^{-i\phi}) + r_1(i\alpha F + r_2(e^{-i\phi} - i\alpha(m + 1))] = -i\alpha F,$$

(25)

$$a_1(1 + i\alpha c e^{i\phi}) + a_2(i\alpha F e^{i\phi}) + b_1(1 - i\alpha c e^{-i\phi}) - b_2(i\alpha F e^{-i\phi}) + r_1(1 + i\alpha c e^{i\phi}) - r_2(1 - i\alpha(m + 1)e^{-i\phi}) = i\alpha F e^{i\phi}.$$  

(26)

and

$$a_2(i\alpha F e^{i\phi} + a_2[1 - i\alpha(m + 1)e^{i\phi}] + b_2(1 + i\alpha(m + 1)e^{-i\phi}) + r_1(i\alpha F e^{i\phi}) - r_2(1 - i\alpha(m + 1)e^{-i\phi}) = i\alpha F e^{i\phi}.$$  

(27)

Here, $\alpha = J/\hbar v_F$. The mixing of the spin-up and spin-down components in the above equations is attributed to the exchange operator $\mathbf{s} \cdot \mathbf{S}$.

At $x = a$, the boundary conditions are given as

$$-i\hbar v_F [\psi_B^I(x = a^+) - \psi_B^I(x = a^-)] = \frac{\hbar}{2} [\psi_B^I(x = a^+) + \psi_B^I(x = a^-)]$$

and

$$-i\hbar v_F [\psi_A^I(x = a^+) - \psi_A^I(x = a^-)] = \frac{\hbar}{2} [\psi_A^I(x = a^+) + \psi_A^I(x = a^-)],$$

which lead to

$$a_1 e^{i\phi}(iG - e^{i\phi}) + b_1 e^{-i\phi}(iG + e^{-i\phi}) + r_1 e^{i\phi}(e^{i\phi} + iG) = 0,$$

(28)

$$a_2 e^{i\phi}(1 + iGe^{i\phi}) - b_1 e^{-i\phi}(1 + iGe^{-i\phi}) + r_1 e^{i\phi}(1 + iGe^{i\phi}) = 0,$$

(29)

$$a_2 e^{i\phi}(1 + iGe^{i\phi}) - b_1 e^{-i\phi}(1 + iGe^{-i\phi}) + r_1 e^{i\phi}(1 + iGe^{i\phi}) = 0,$$

(30)

and

$$a_2 e^{i\phi}(1 + iGe^{i\phi}) - b_1 e^{-i\phi}(1 + iGe^{-i\phi}) + r_1 e^{i\phi}(1 + iGe^{i\phi}) = 0,$$

(31)

where $G = V(2\hbar v_F)$.

The equations (24)–(31) contain eight unknown probability amplitudes, which can be solved numerically to confirm $|\alpha|^2 + |\beta|^2 + |\gamma|^2 + |\delta|^2 = 1$. Similarly for the case of a spin-down electron incident from the left side, we can get scattering amplitudes. This procedure can be repeated appropriately for spin-up/down electron coming from the right side.

III. Results and discussions

Different components of quantum pumped currents, i.e. spin-up ($I_1$), spin-down ($I_2$) and net spin current ($I_z = I_1 - I_2$) and charge current ($I_c = I_1 + I_2$), are obtained numerically using equation (12) at zero temperature as shown in figures 2(a)–(d). Figures 2(a) and (b) show the quantum pumped currents ($I_1, I_2, I_z, I_c$) versus energy of the incident electron ($E$) and strength of adatom/line defect for weak pumping, without disorder. The following numerical parameters are used (mentioned in the figure also): the spatial separation between the SMM and the adatom $a = 10$ nm, the strength of exchange interaction between the electron and the molecular magnet $J = 0.3$ eV nm, $m = -1/2$ and spin of the molecular magnet $S = 3/2$. The strength of the line defect potential $V = 0.3$ eV nm and the strength of the time-varying modulations on top of $V$ and $J$ are taken as $x_p = 0.05$ eV nm in the strong pumping case. From figure 2(a), it is seen that for a suitable energy $E$ ($\approx 54$ meV), the total charge current completely disappears, leaving behind a pure spin current. Figure 2(b) shows that individual spin-pumped currents vary slowly with increasing ordinary potential. $I_1$ is decreasing while $I_2$ is increasing with $V$. The pumped currents in the weak pumping regime are in units of $I_0$ as in equation (8), while those in the strong pumping regime are in units of $\pi e\hbar/2\tau$. Another important point in the weak pumping case is that, by suitably choosing $E$, $I_z$ can be completely suppressed to pump only $I_1$, a spin-up selective current.

Figures 2(c) and (d) are plotted to check how the strength of the exchange interaction ($J$) affects the different pumped currents. We have taken the energy of the incident electron ($E \approx 54$ meV) for which pure spin current was observed. From figure 2(c), we see that the pumped currents attain a maximum around $J = 0.1$ and $-0.13$ eV nm and then start diminishing towards zero; pure spin current appears at $J = 0.3$ eV nm, and spin-selective current $I_z$ appears for $J > 0.5$ eV nm. However, in strong pumping as shown in figure 2(d), pure spin current appears at the same position at $J = 0.3$ eV nm. For both weak and strong pumping plots, we have chosen the phase difference between two modulations as $\pi/2$. One important fact that is clearly noticeable is that $J$ acts as a current switch. By
changing $J$ from positive to negative, all the pumped currents change sign. This shows that the magnetization of the SMM controls the direction of current flow in graphene. Since we aim to control this by the twist, effectively twisting the SMM changes the direction of spin currents. This is a key result of our work.

III.A. Effect of disorder and temperature

In this section, we discuss the effects of disorder distributed randomly in the system. We have modeled the present device in such way that the SMM and adatom/line defect are at the extreme ends of the sample and disorder is confined between the SMM and adatom/line defect. Here each disorder is considered to be a delta potential (a point interaction as mentioned before). We solve this problem by using the transfer matrix approach. The presence of multiple delta potentials creates a number of confined regions between the SMM and the adatom. The general form of the wavefunction in each region can be written as

$$
\psi_n(x) = \frac{1}{2}\left( A_n e^{i k x} + B_n e^{-i k x} \right) \chi_m \left( A_n e^{i k x} + B_n e^{-i k x} \right) \chi_{m+1}.
$$

Here $n = 0, 1, 2, 3, \ldots, (N - 1), N$ corresponding to different regions bounded by the delta potentials, as shown in figure 3. The above wavefunction is for sublattice $A$; the phase factor $\exp(\pm i\phi)$ is multiplied by the transmission (reflection) amplitude to get the same for sublattice $B$. The next step is to find the total transfer matrix that connects the wavefunction amplitudes between extreme left and right. To do so, first we find the transfer matrix across the SMM, i.e. between regions ‘$n = 0$’ and ‘$n = 1$’ as in figure 3,

$$
\begin{bmatrix}
A_1^* \\
A_1 \\
B_1^* \\
B_1
\end{bmatrix} = M^{(1,0)}
\begin{bmatrix}
A_0^* \\
A_0 \\
B_0^* \\
B_0
\end{bmatrix}.
$$

Figure 2. Pumped spin currents at zero temperature. (a) Quantum pumping current versus energy of incident electron for weak pumping. (b) Quantum pumping current versus strength of the delta-like point interaction for weak pumping. (c) Weak pumping: quantum pumping current versus strength of the molecular magnet. (d) Strong pumping: quantum pumping current versus strength of the molecular magnet.
where $M_{[1,0]}^{[1,0]}$ is the transfer matrix across the SMM, expressed as $M_{[1,0]}^{[1,0]} = M_f/M_0$ with

$$
M_0 = \begin{bmatrix}
\xi - i\alpha \xi & \xi - i\alpha \xi \\
i\alpha F & -i\alpha F \\
l & l + i\alpha \xi & l + i\alpha \xi \\
i\alpha F \xi & 1 + i\alpha (m + 1) \xi & 1 + i\alpha (m + 1) \xi \\
\xi + i\alpha \xi & i\alpha F \xi & i\alpha F \xi \\
i\alpha F \xi & 1 + i\alpha (m + 1) \xi & i\alpha F \xi
\end{bmatrix}
$$

(34)

and

$$
M_1 = \begin{bmatrix}
\xi + i\alpha \xi & \xi - i\alpha \xi \\
i\alpha F & i\alpha F \\
l & l - i\alpha \xi & l - i\alpha \xi \\
i\alpha F \xi & 1 - i\alpha (m + 1) \xi & 1 - i\alpha (m + 1) \xi \\
i\alpha F \xi & 1 - i\alpha (m + 1) \xi & i\alpha F \xi
\end{bmatrix}
$$

(35)

with $\xi = \exp(i\phi)$ and $\xi = \exp(-i\phi)$. Similarly we can get the transfer matrix across any arbitrary potential, for example the transfer matrix between 'n = N' and 'n = N - 1' as

$$
\begin{bmatrix}
A_N^+ \\
B_N^+
\end{bmatrix} = M_{N,N-1}^T
\begin{bmatrix}
A_{N-1}^- \\
B_{N-1}^-
\end{bmatrix}
$$

(36)

where $M_{N,N-1}^{[N,N-1]}$ is the transfer matrix across the adatom, expressed as $M_{N,N-1}^{[N,N-1]} = M_f/M_{N-1}$ with

$$
M_{N-1} = \begin{bmatrix}
\xi - iG & 0 & iG - \xi & 0 \\
0 & \xi - iG & 0 & iG - \xi \\
l - iG \xi & 0 & 1 + iG \xi & 0 \\
0 & 1 - iG \xi & 0 & 1 + iG \xi
\end{bmatrix}
$$

(37)

and

$$
M_N = \begin{bmatrix}
\xi + iG & 0 & iG - \xi & 0 \\
0 & \xi + iG & 0 & iG - \xi \\
l + iG \xi & 0 & 1 - iG \xi & 0 \\
0 & 1 + iG \xi & 0 & 1 - iG \xi
\end{bmatrix}
$$

(38)

Since the adatom is modeled as a delta function potential and disorder is modeled too as a randomly distributed sequence of delta potentials with random strengths, the transfer matrix for any arbitrary interface between the adatom and SMM has also the same matrix elements as $M_{N,N-1}^{[N,N-1]}$.

After some straightforward algebra, the connection between the wavefunction amplitudes of extreme left and right is found to be [20]

$$
\begin{bmatrix}
A_N^+ \\
B_N^+
\end{bmatrix} = M
\begin{bmatrix}
A_0^+ \\
B_0^+
\end{bmatrix},
$$

(39)

where

$$
M = M_{[N,N-1]}^{[N,N-1]}M_{[N-1,N-2]}^{[N-1]}\cdots M_{[1,0]}^{[1,0]}M_{[1,1]}^{[1,1]}M_{[1,2]}^{[1,2]},
$$

(40)

and $M_{[1,1]}$, the propagation matrix between any two successive delta potentials, is given by

$$
M_{[1,1]}^{[1,1]} = \begin{bmatrix}
e^{ild_0} & 0 & 0 & 0 \\
0 & e^{ild_0} & 0 & 0 \\
0 & 0 & e^{-ild_0} & 0 \\
0 & 0 & 0 & e^{-ild_0}
\end{bmatrix}
$$

(41)

Here, $d_0$ is the separation between two consecutive delta potentials. To calculate the reflection and transmission amplitudes, we shall use the scattering matrix (S-matrix), which is connected to the transfer matrix as [20]

$$
S = \frac{1}{(M_{[1,2]}^{[1,2]})_{2\times2}}[(M_{[1,2]}^{[1,2]})_{2\times2}^{-1}\det(M)]
$$

(42)

The reflection amplitude (to the left, as we are calculating pumped currents in the left lead) is

$$
r_1 = -\frac{M_{11}^{[1,1]}}{M_{22}^{[1,1]}}\begin{bmatrix} r_{11}^{[1,1]} & r_{12}^{[1,1]} \end{bmatrix}
$$

(43)

and the transmission amplitude from right to left is

$$
t_1 = \frac{1}{M_{22}^{[1,1]}}\begin{bmatrix} t_{11}^{[1,1]} & t_{12}^{[1,1]} \end{bmatrix}
$$

(44)

t_1 and $r_1$ can be used directly in equation (13) to obtain the quantum pumped currents. We must mention here that the disorder-free pumping current can also be recovered from here by using the transfer matrix as $M = M_{[1,1]}^{[1,1]}M_{[1,2]}^{[1,2]}M_{[1,3]}^{[1,3]}$, where $M_{[1,1]}^{[1,1]}$ and $M_{[1,3]}^{[1,3]}$ would become the transfer matrix across the adatom and SMM, respectively.

The effect of disorder is shown in figure 4(a). Herein we plot the pumped currents as functions of the different spin states of the SMM in the weak pumping regime. There is pure spin current for $S = 3/2$ in the figure with $m = -1/2$. To include disorder, we have chosen the random spacing between any two potentials in the range $1–1.5$ nm. The strength of the potential is also random and ranges from 50–100 meV-ang (dashed line) to 100–200 meV-ang (dashed–dot line). We have considered the pumped currents averaged over 1000 realizations. One can see that disorder has a limited effect on the pure spin current. The position of the pure spin current is shifted from $S = 3/2$ (without disorder) to $S = 5/2$ (disorder: 50–100 meV-ang) and finally $S = 7/2$ (disorder: 100–200 meV-ang); however, pure spin currents are not killed off. In figure 4(b) we see the effect of
disorder on pumped currents plotted as a function of the magnetization of the SMM. We again see that the position of occurrence of pure spin current \( I_c = 0 \) changes from \( J = 0.3 \) to 0.45 eV nm as one increases disorder. However, disorder has no effect on magnetization switching of pumped spin currents, showing the resilience of the magnetization switching to disorder.

Finally, in figure 5 we plot the pumped currents as a function of the phase difference between modulated parameters. We see that the pumped current attains a maximum at \( \theta = \pi/2 \) and minima around \( \theta = 0 \) and \( \pi \). The pure spin current is maintained throughout the whole range of \( \theta \). The temperature effect is shown in the same figure, and shows a small damping in amplitudes of the individual spin currents. One can see that temperature has no noticeable effect on the pure spin currents apart from a slight diminishing of the magnitude. To conclude this section, pure spin currents in graphene are immune to any increase in temperature apart from a decrease in magnitude, while disorder has a small effect as it shifts the parameter regime for the occurrence of pure spin currents although it cannot kill it off.

IV. Pumping versus rectification

A major issue that was flagged right from the early days of quantum pumping was whether the Switkes experiment [5] was a real demonstration of quantum pumping, since the pumped current was observed to be symmetric with respect to magnetic field reversal just like the two-terminal conductance [25]. However, since pumped currents are functions of scattering amplitudes and not scattering probabilities they should have no particular symmetry with respect to magnetic field reversal unless the system itself has some particular symmetry [26]. As the Switkes experimental system did not possess any particular symmetry it was quickly recognized that the current attributed as a pumping current was in effect a rectified current that depend on the conductance of the system [27]. However, there could have been a pumped current that was masked by the rectified currents. Rectified currents arise because experimentally at the nanoscale it is difficult to control time-varying parameters. Most naturally time-varying parameters couple to input and output leads, and instead of pumping only a current there is in addition a transport current defining the net conductance through the system. So any quantum pumping at the nanoscale will have rectified currents and therefore it become imperative to have a scheme to differentiate these currents. The rectified spin-up current is defined as

\[
I_{\text{rect}} = \frac{1}{2\pi} \int \frac{d\theta}{\sin \theta} X_0 \left( C_1 \frac{\partial G}{\partial \theta} - C_2 \frac{\partial G}{\partial \theta} \right),
\]

where \( X_0 \) are the modulated parameters. In the weak pumping regime we have

\[
I_{\text{rect}} = I_0 \left( C_1 \frac{\partial G}{\partial \theta} - C_2 \frac{\partial G}{\partial \theta} \right) \sin \theta.
\]

In figure 6 we can see clearly that the conductance (both spin-up and spin-down) is symmetric with respect to small values of \( J \). Thus unlike pumped currents, whose direction can be change by changing the magnetization from positive to negative, the conductance shows no such effect. The pumped currents are completely asymmetric as a function of \( J \) as seen in figures 2(c) and (d). Thus even if rectified currents are present in the system the pumped spin current will be distinguished because of its asymmetric nature with respect to magnetization reversal.

V. Experimental realization and conclusions

Experimental realization of our pure spin current pumping device should not be too difficult. As already outlined in the last paragraph of the introduction of this paper, adiabatically modulating the pressure applied on the single-molecule magnet would entail a corresponding adiabatically modulated magnetization of the SMM. The second adiabatically modulated parameter of the device is an adatom placed a distance \( a \) apart from SMM. The adatom is modeled as a delta function-like point interaction similarly embedded in graphene. A gate voltage applied to the adatom can change the potential felt by electrons scattered from it. When the gate voltage itself is adiabatically modulated in time we have all the ingredients for...
Pumped currents with spin up and down are asymmetric. Compare with figures 2(c) and (d). The solid line is for zero temperature while the dashed line is for finite temperature.

Figure 5. Quantum pumping current versus phase angle between two modulations for strong pumping. The solid line is for zero temperature while the dashed line is for finite temperature.

Figure 6. Conductance (spin up and spin down) versus $J$. $G$ is symmetric for small $J$ values. Compare with figures 2(c) and (d). Pumped currents with spin up and down are asymmetric.

The quantum pumping of pure spin currents and spin-selective currents. Alternatively, an extended line defect can be created instead of an adatom, which can be controlled experimentally [22–24]. Moreover, one can also use a thin potential barrier which can be theoretically modeled as a delta-like potential. Similarly, the single-molecule magnet is in fact a large molecule consisting of a host of 30–100 atoms, these atoms being arranged such that they have not only a vertical but also a horizontal extent, i.e. a single-molecule magnet will have a significant extent in the transverse direction. Mention may be made of [28] on single-molecule magnets, which exemplifies the situation envisaged.

To conclude, although spin transport via the spin–orbit effect is almost impossible to observe in graphene, we have created in a novel manner pumped pure spin currents and spin-selective currents in graphene by embedding it with a single-molecule magnet. The study of pure spin currents in graphene via an embedded SMM will be extended in a subsequent work to spin correlations and to whether one can generate entangled spin currents that will have a potential impact on quantum information processing.

Acknowledgments

The authors acknowledge useful discussions with Purbasha Sharangi on the disorder effects included. Colin Benjamin thanks the Department of Science and Technology (Nano-mission), Govt. of India for funds under Grant No. SR/NM/NS-1101/2011.

References

[1] Katsnelson M I, Novoselov K S and Geim A K 2006 Nat. Phys. 2 620–5
[2] Novoselov K S et al 2007 Science 315 1379
[3] Inglis R, Milios C J, Jones L F, Piligkos S and Brechin E K 2012 Chem. Commun. 48 181
[4] Brouwer P W 1998 Phys. Rev. B 58 R10135
[5] Switkes M et al 1999 Science 283 1905
[6] Benjamin R and Benjamin C 2004 Phys. Rev. B 69 085318
[7] Watson S K, Potok R M, Marcus C M and Umansky V 2003 Phys. Rev. Lett. 91 258301
[8] Zutic I, Fabian J and Das Sarma S 2004 Rev. Mod. Phys. 76 323
[9] Tombros N et al 2007 Nature 448 571
[10] Guimeraes M H D et al 2014 Phys. Rev. B 80 214427
[11] Zhang Q, Chang K S and Lin Z J 2011 Appl. Phys. Lett. 98 032106
Zhang Q, Chang K S and Lin Z J 2012 J. Phys.: Condens. Matter 24 075302
[12] Gatteschi D and Sessoli R 2003 Angew. Chem. Int. Ed. 42 268
[13] Wernsdorfer W et al 2002 Phys. Rev. B 65 180403
[14] Milios C J, Vinslava A, Wood P A, Parsons S, Wernsdorfer W, Christou G, Perlepes S P and Brechin E K 2007 J. Am. Chem. Soc. 129 6547
[15] Precesimone A et al 2008 Angew. Chem. Int. Ed. 47 2828
[16] Brechin E K 2015 private communication
[17] Misiorny M and Barnas J 2007 Phys. Rev. B 76 054444
[18] Castro A H, Guinea F, Peres N M R, Novoselov K S and Geim A K 2009 Rev. Mod. Phys. 81 109
[19] Moskalets M and Buttiker M 2002 Phys. Rev. B 66 205320
[20] Griffiths D J and Steinke C A 2001 Am. J. Phys. 69 137
[21] Cordourier-Maruri G, Omar Y, de Coss R and Bose S 2014 Phys. Rev. B 89 075426
[22] Lahiri J et al 2010 Nat. Nanotechnol. 5 326
[23] Li X et al 2011 J. Am. Chem. Soc. 133 2816
[24] Chen J H et al 2014 Phys. Rev. B 89 121407
[25] Brouwer P W 2001 Phys. Rev. B 63 121303
[26] Shutenko T A, Aleiner I and Altshuler B 2000 Phys. Rev. B 61 10366
[27] Benjamin C 2006 Eur. Phys. J. B 52 403
[28] Benjamin C 2013 Appl. Phys. Lett. 103 043120
[29] Bogan I and Wernsdorfer W 2008 Nat. Mater. 7 179