Spin selective transport through helical molecular systems

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Abstract

Highly spin selective transport of electrons through a helically shaped electrostatic potential is demonstrated in the frame of a minimal model approach. The effect is significant even in the case of weak spin-orbit coupling. Two main factors determine the selectivity, an unconventional Rashba-like spin-orbit interaction, reflecting the helical symmetry of the system, and a weakly dispersive electronic band of the helical system. The weak electronic coupling, associated with the small dispersion, leads to a low mobility of the charges in the system and allows even weak spin-orbit interactions to be effective. The results are expected to be generic for chiral molecular systems displaying low spin-orbit coupling and low conductivity.

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Introduction. The concept of spintronic devices operating without a magnetic field has been proposed some time ago for solid state devices in which the spin-orbit coupling (SOC) is large.\textsuperscript{1,2} Recently, a new type of magnet-less spin selective transmission effect has been reported. It was found that electron transmission through chiral molecules is highly spin selective at room temperature.\textsuperscript{3-6} These findings are surprising since carbon-based molecules have typically a small SOC that cannot support significant splitting between the spin states, splitting which is thought to be essential for any spin dependent property. Although it has been found both in theory\textsuperscript{7-9} and experiments\textsuperscript{10} that there is a cooperative contribution to the value of the SOC, so that this quantity may be larger in molecules or nanotubes than in a single carbon atom, the values calculated or experimentally found are still relatively small,\textsuperscript{7-11} e.g. for carbon nanotubes the SOC is of the order of few meV.\textsuperscript{10} Hence, even including this cooperative contribution, the values obtained for the spin polarization (SP) in electron transmission through chiral molecules\textsuperscript{6} seem to be extremely high.

A theoretical model has been proposed for explaining the spin selectivity of chiral molecules. It involves the introduction of Rashba type\textsuperscript{11,12,13,14} SOC for electron-chiral molecule scattering.\textsuperscript{15} The results are in qualitative agreement with the experimental observation but it does not able to explain them quantitatively.

In what follows a model is presented to describe electron transmission through a helically shaped electrostatic potential (see Figure 1). Even though the model does not claim to fully catch the complexity of the experimentally studied DNA-based systems,\textsuperscript{16} it focuses on important parameters and the obtained results indicate which mechanisms may be involved in the high SP observed. It turns out that the main contributions to the selectivity result from electrons with velocities near the energy band edge.

The key factors in the model that allow for the high spin selectivity are: i) Breaking of the parity symmetry due to the chiral nature of the potential; ii) Narrow electronic band widths of the helical system. Namely, the interaction between the units composing the helical structure through which the electron propagates is relatively weak, resulting in low mobility and expected long residence times of the electron in the system; iii) Like in solid state cases, also in the present study, the electric potential acting on the electron has to include the interaction of the transmitted electron with many electrons on each atom;\textsuperscript{17} iv) Due to proximity effects (and the lack of inversion symmetry), the Coulomb interaction between the transmitted electron and the atoms in the molecule can scale as $1/R$ for short distances $R$. 
Figure 1. A charge $q$ in spin state $\sigma$ is moving with velocity $v$ along the axis of a helical charge distribution. The parameters $b$ and $\Delta z$ are the pitch of the helix with radius $a$, and the spacing of the $z$-component of the position vector of the charges distributed along the helix, respectively. The helical electric field, $E_{\text{helix}}$, induces a magnetic field $B$ in the rest frame of the charge and hence influences its spin state.

Model and Methodology. We consider the Schrödinger equation for a particle moving in a helical electrostatic field. Analytical results for such fields have been derived in Ref. 12. For the sake of simplicity, approximate expressions valid near the $z$-axis will be used (only $x$ and $y$ field components will be considered, since the $z$-component, as indicated in Ref. 12, is small):

$$E_{\text{helix}} = -E_0 \sum_{i,j} g_{ij} \left( \cos(Qi\Delta z) \sin(Qj\Delta z) \right).$$

Here, $g_{ij} = 1/2 \left( a^2 + (z - ib - j\Delta z)^2 \right)^{3/2}$ and $Q = 2\pi / b$ with $b$ being the helix pitch and $a$ the helix radius, see Fig. 1. The index $j$ runs along one helical turn and labels the $z$-coordinate of point charges placed along the helix. The index $i$ runs over the $L$ turns of the helix and connects charges placed at sites which differ in their $z$-coordinate by a pitch length. We chose $b=3.2$ nm, $a=1$ nm, and $\Delta z=0.32$ nm, values which are close to those of B-DNA. The factor $E_0$ is proportional to the local charge density and it will be estimated below.

For a charge propagating with momentum $p$ through the helix, the helical field $E_{\text{helix}}$ induces a magnetic field in the charge’s rest frame, from which an SOC arises: $H_{\text{soc}} = \lambda \sigma (p \times E_{\text{helix}})$. When $\lambda = \epsilon h / 4m^2 c^2$ and $\sigma$ is a vector whose components are the Pauli spin matrices $\sigma_x, \sigma_y, \sigma_z$. The problem is three-dimensional; however, in order to get first insights into the behavior of the SP, we will assume $p_x = p_y = 0, p_z \neq 0$, so that the Schrödinger equation with the SOC Hamiltonian takes the form:

$$\begin{pmatrix} -\frac{\hbar^2}{2m} \partial_z^2 + \alpha \left( -\Psi(z) \partial_z - f(z) \right) \Psi(z) \partial_z - f(z) \end{pmatrix} \chi(z) = E \chi(z).$$

(1)
Here \( \chi(z) = \left( \chi^+ (z), \chi^- (z) \right) \) is a two-components spinor, \( \Psi(z) = \sum_{n,m} e^{iQn\Delta z} (1 + u_{nm}^2)^{-1/2} f(z) = \partial_z \Psi(z) \) and \( u_{nm} = (z - bn - m\Delta z)/a \). The terms \( f(z), f^*(z) \) in Eq. (1) is introduced to make the Hamiltonian hermitian in the continuum representation. The SOC parameter \( \alpha \) (with dimensions of energy x length) is given by: \( \alpha = \hbar \lambda E_0 \), and it depends on the effective charge density through \( E_0 \). The problem posed by Eq. (1) can be written as an effective two-channel nearest-neighbor tight-binding model:

\[
H = V \sum_{\sigma = \uparrow, \downarrow} \sum_{n=1}^N \left( \sigma^+_{n,\sigma} c_{n+1,\sigma}^+ + h.c. \right) + \sum_{n,m=1}^N \left( c_{n,\uparrow}^+ W_{n,m}^\uparrow c_{m,\uparrow}^+ + c_{n,\downarrow}^+ W_{n,m}^\downarrow c_{m,\downarrow}^+ \right) + H_{\text{leads}}. \tag{2}
\]

The operators \( \{ c_{n,\sigma}, c_{n,\sigma}^+ \} \) create or destroy, respectively, an excitation at site \( n \) with spin index \( \sigma \). The only non-zero elements of the inter-channel coupling matrix \( W \) are given by:

\[
W_{n,n} = -\alpha f(n\Delta z), W_{n,n+1} = \alpha \Psi((n-1)\Delta z)/\Delta z, \quad \text{and} \quad W_{n,n-1} = -\alpha \Psi^*((n+1)\Delta z)/\Delta z.
\]

Further, the matrix \( W_{n,m}^\sigma \) satisfies \( W_{n,m}^{\sigma\sigma} = -W_{m,n}^{-\sigma\sigma} \), for \( n \neq m \), and \( W_{n,n}^\sigma = (W_{n,n}^\sigma)^\dagger \). The hopping term \( V \) can be estimated on the basis of a first-principle calculation of electronic coupling matrix elements for a given system. However, we will consider it as a free parameter, whose order of magnitude for helical organic systems is expected to lie in the range of few tens of meV (for DNA, electronic structure calculations yield values of the order of 20-40 meV\(^{19,20} \)) Finally, the term \( H_{\text{leads}} \) includes the semi-infinite chains to the left (L) and right (R) of the SO active region. A schematic representation of the two-channel model is shown on the top panel of Fig. 2.

**Transport properties.** We will focus on the (spin-dependent) transmission probability, \( T(E) \), as a function of the injection energy \( E \) of the electron, which will be computed using Landauer’s theory.\(^{21} \)

A scattering where a finite-size problem is considered, where a finite size region (with non-zero SOC) is coupled to two independent L- and two R-electrodes, each electrode standing for a spin channel and being represented by a semi-infinite chain, see Fig. 2. The transmission function within a nearest-neighbor approximation can be written as:

\[
T(E) = \Gamma^\uparrow (G^\downarrow | G_{\uparrow\uparrow} | G_{\downarrow\uparrow} | G_{\downarrow\downarrow} |) + \Gamma^\downarrow (G^\uparrow | G_{\uparrow\uparrow} | G_{\downarrow\uparrow} | G_{\downarrow\downarrow} |) = t_{\text{up}}(E) + t_{\text{down}}(E). \tag{3}
\]

In Eq. (3), \( G_{\sigma,\nu,v}(E) \) with \( \sigma,\nu = \uparrow, \downarrow \) are matrix elements of the retarded Green’s function of the SOC region including the influence of the L- and R-electrodes. The individual contributions in Eq. (3) can be related to different transport processes without (e.g. \( \Gamma^\uparrow | G_{\uparrow\uparrow} | G_{\downarrow\uparrow} | G_{\downarrow\downarrow} | \)) or with (e.g. \( \Gamma^\downarrow | G_{\uparrow\uparrow} | G_{\downarrow\uparrow} | G_{\downarrow\downarrow} | \)) spin flip scattering, see also Fig. 2. Notice that \( t_{\text{up}}(E) \) and \( t_{\text{down}}(E) \) -the transmissions for up and down channels respectively, as defined by Eq. (3), contain contributions arising both from direct transmission without spin-flip as well as spin-flip. An energy-resolved SP for different initial spinor states can further be defined:

\[
P(E) = \left( t_{\text{up}}(E) - t_{\text{down}}(E) \right)/T(E).
\]

For the discussion below, energy-
averaged SPs $\langle P(E) \rangle_E = P(\langle t_{\text{up}} \rangle_E, \langle t_{\text{down}} \rangle_E, \langle T(E) \rangle_E)$ will also be used. We focus only on electron-like contributions ($E < 0$) and on energies with $|E| \geq k_B T \approx 23 \text{ meV}$, so that $< ... >_E = \int_{-k_B T}^{k_B T} dE(...)$.

**Results.** A crucial parameter in the present model is the SOC coupling strength $\alpha$. Realistic values are difficult to obtain, since $\alpha$ is not simply the atomic SOC, but contains the influence of the charge distribution in the system via the field factor $E_0$. A rough estimate of $E_0$ for a molecule like DNA may be obtained along the following lines. A single DNA base may be considered as composed of discrete point-like charge centers $A$, representing the atoms. We associate with each center $A$ at position $R_A$ a Gaussian-shaped charge distribution with width $w$ of roughly the radius of a base (~0.3-0.4 nm) and with strength given by the estimated atomic charge density $\rho_0$ for C, O, and N atoms (considered as spheres with a radius of the order of the corresponding covalent radius). The local field of this charge distribution (ignoring for the moment the interaction with the other centers),

$$E_0 = \left(1/4 \pi \rho_0 \right) \int d^3r \rho_0(r - R_A) |r - r'|^{-1},$$

can be computed analytically and it scales for $R = |r - R_A| \ll \alpha$ like $E_0 \approx N(1/4 \pi \rho_0)(w/2\sqrt{\pi})^2 \rho_0 R^{-1}$. We have multiplied $E_0$ by a factor $N \approx 10$ (the number of atoms in a base) to approximately account for other charge centers. For $R \approx 0.1 \text{ nm}$, a value of $\alpha = h \lambda E_0 \approx 2.35 \text{ meV nm}$ is obtained. In the following calculations, values of $\alpha = 2-6 \text{ meV nm}$ will be used. Though being a rough estimate, it highlights the need of considering the influence of many charges through $E_0$ as well as proximity effects when calculating the SOC. These values are in agreement with those observed experimentally for carbon-based supramolecular structures like carbon nanotubes.$^{10}$

Figure 2 presents the energy dependent SP for different incoming spin states when the spin is pointing, up (10), down (01) or the electrons are unpolarized (11). The SOC coupling $\alpha$ was assumed to be 5 meV nm. Although this value is larger than the previously estimated one, it serves to illustrate the behavior of the model in a clear way. The assumed hopping $V = 20 \text{ meV}$ is of the order of what is typically obtained for stacked biomolecules like DNA. In the case of (10) and (01) initial conditions, the interesting energy window is where both SPs have the same sign, since this indicates that the outgoing state will have always the same SP independently of the initial condition. This behavior occurs for energies near the band edges. A similar situation is found for the (11) state, see the behavior of $P_{11}(E)$ in Fig. 2. Near the band center, although $P(E)$ is in general different from zero, $P_{00}(E)$ and $P_{01}(E)$ have opposite signs and hence there is a dependence on the initial state. The average SPs, as defined above, amount to approximately $<P_{10}>_E = <P_{01}>_E = <P_{11}>_E \approx -80\%$. 


Figure 2. **Top panel:** Schematic representation of the tight-binding model, see Eq. (2). The two channels interact via SOC (framed region). To the left and right of the spin scattering region, both channels are independent and are modeled by semi-infinite chains. **Bottom panel:** Energy dependence of $P(E)$ for three helical turns, and for injected electrons polarized with their spin pointing up ($P_{10}$), down ($P_{01}$), or unpolarized ($P_{11}$). A spin-filter effect takes place for energies near the band edges, where all $P(E)$ have the same sign. Notice also that near the band edges the SP has opposite signs for electrons ($E<0$) and holes ($E>0$), although $P(E)$ is not exactly antisymmetric. Parameters: $\alpha=5$ meV nm, $V'=20$ meV, $L=3$.

Figure 3 shows the corresponding spin-resolved transmission. In what follows, only the behavior of electron-like contributions ($E<0$) is discussed. Notice first, that the states (10) and (01) correspond to cases where one of the incoming spin channels is decoupled from the system by setting the corresponding $\Gamma^L=0$, and hence, the total transmission cannot exceed one. For (11) both channels are open and the maximum transmission is 2. In the top panel of Fig. 3, for (10) and (01) we find a certain degree of spin-dependent back-scattering, which is reflected in the different total transmissions $T(E)$ for each polarization. The relative difference between the transmissions for (10) and (01) was estimated to be of about 10-15%. At energies near the lower band edge, the outgoing down channel has always a higher transmission ($t_{\text{down}}$) and hence $P_{10}$ and $P_{01}$ become negative. Hence, for the (10)
state, spin-flip and (partially) spin-selective scattering lead to a higher population of the outgoing spin-down channel. For the (11) state, bottom panel of Fig. 3, a progressive increasing of back-scattering and spin-flip of the up-spin when moving towards the negative band edge also leads to a negative SP.

Figure 3. Energy dependence of the different components of the transmission $t_{up}(E)$, $t_{down}(E)$, and $T(E)$, as defined in Eq. (3), for the parameters given in Fig. 2. Focusing on electron-like contributions, it is only near the lower band edge ($E \leq -20$ meV) where for the (10), (01), and (11) states, $t_{up}(E)$ is strongly suppressed, and as a result, a negative SP for all incoming states is obtained in that energy region, see also Fig. 2. Parameters: $\alpha=5$ meV nm, $V=20$ meV, $L=3$.

In general terms, SP may ideally occur either by spin-flip processes (with no net change of the total transmission) or by spin selective back-scattering. The results of Fig. 3 suggest that both processes are playing a role, their relative contribution depends however sensitively on the specific energy window considered. The selectivity found in this model relates to two special features of the chiral system: (i) the symmetry of the field which translates into an unconventional SOC, and (ii) the narrow electronic band width in chiral organic systems. The term band width serves only as a keyword for the averaged value of the coupling matrix elements, $V$, between neighboring molecular states mediating charge motion.20 As shown in the 2D plot of Fig. 4, the increase of the hopping parameter strongly suppresses the SP, ultimately leading to $<P(E)>_E \rightarrow 0$ for large $V$. For fixed, but not too large $V$, increasing the SOC strength clearly leads to a strong SP increase. The interplay between $\alpha$ and $V$ is related to the relatively long time (roughly proportional to $\hbar V^{-1}$) the electron is spending in the conducting channel, allowing for the SOC to become more effective.
Figure 4. 2D plot of the energy average SP \(<P(E)>_E\) as a function of both the hopping parameter \(V\) and the SOC \(\alpha\). Only for small \(V\) and values of \(\alpha \geq 0.5 \text{–} 0.6 \text{ meV nm}\), a large SP is found. With increasing electronic coupling, larger SOC strengths are required to get a sizeable SP.

**Conclusions.** The present study based on a minimal model approach sheds new light on a chirality-induced spin selectivity (CISS) effect. It suggests that beyond the symmetry itself, CISS depends on the organic molecules being poor conductors. The weak electronic coupling along the helical structure is expected to lead to low mobility of the electrons through the system in real systems and allows enough time for the SOC, although being weak, to influence the transport. The effect depends on the electron momentum and once the electrons injected have kinetic energy above \(k_B T\), the SP increases and then becomes weakly energy independent. One open issue for further inquiry is the influence of the electrode-molecule interface. If the electrodes are magnetic, spin-dependent tunnel barriers emerge and this may influence the observed SP. The present study indicates that CISS may be a very general phenomenon, existing in chiral systems having low SOC and low conductivity, and hence may play a role in electron transport through biological systems.

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References

18. Details of the theoretical model are provided in the Supplementary Material.