Spin-Selective Transport of Electron in DNA Double Helix

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The experiment that the high spin selectivity and the length-dependent spin polarization are observed in double-stranded DNA [Science 331, 894 (2011)], is elucidated by considering the combination of the spin-orbit coupling, the environment-induced dephasing, and the helical symmetry. We show that the spin polarization in double-stranded DNA is significant even in the case of weak spin-orbit coupling, while no spin polarization appears in single-stranded DNA. Furthermore, the underlying physical mechanism and the parameters-dependence of the spin polarization are studied.

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Molecular spintronics, by combining molecular electronics with spintronics to manipulate the transport of electron spins in organic molecular systems, is regarded as one of the most promising research fields and is now attracting extensive interest [1–4], owing to the long spin relaxation time and the flexibility of organic materials. Unconventional magnetic properties of molecular systems reported in organic spin valves and magnetic tunnel junctions, are attributed to the hybrid states in the organic-magnetic interfaces [5–9] and to single-molecule magnet [10]. Organic molecules would not be suitable candidates for spin-selective transport because of their nonmagnetic properties and weak spin-orbit coupling (SOC) [10].

However, very recently, Göhler et al. reported the spin selectivity of photoelectron transmission through self-assembled monolayers of double-stranded DNA (dsDNA) deposited on gold substrate [11]. They found that well-organized monolayers of the dsDNA act as very efficient organized monolayers of the DNA exhibit high spin polarization, the spin filtration efficiency increases by increasing the DNA length, and no spin polarization appears for the ssDNA. The physical mechanism arises from the combination of the dephasing, the SOC, and the helical symmetry. No spin polarization could be observed if any aforementioned factor is absent. In addition, the spin polarization could be considerably enhanced by appropriately increasing the dephasing strength or by decreasing the helix angle.

The charge transport through the dsDNA, illustrated in Fig. 1, can be simulated by the Hamiltonian:

$$H = H_{\text{DNA}} + H_{\text{lead}} + H_{c} + H_{\text{so}} + H_{d}. \quad (1)$$

Here $H_{\text{DNA}} = \sum_{n=1}^{N} \sum_{j=1}^{2} (\varepsilon_{jn} c_{jn}^{\dagger} c_{jn} + t_{jn} c_{jn}^{\dagger} c_{jn+1} + \lambda_{n} c_{jn}^{\dagger} c_{jn} + \text{H.c.})$ is the Hamiltonian of usual two-leg ladder model including spin degree of freedom [17], with $N$ the DNA length, $\varepsilon_{jn} = (\varepsilon_{jn1}, \varepsilon_{jn2})$ the creation operator of the spinor at the $n$th site of the $j$th chain of the dsDNA, $\varepsilon_{jn}$ the on-site energy, $t_{jn}$ the intrachain hopping integral, and $\lambda_{n}$ the interchain hybridization interaction. $H_{\text{lead}} + H_{c} = \sum_{k,\beta} (\beta=L,R) \varepsilon_{jk} a_{j \beta k}^{\dagger} a_{j \beta k} + t_{jk} a_{j \beta k}^{\dagger} (c_{j-n} + c_{2n}) + \text{H.c.}$ describe the left and right nonmagnetic leads and the coupling between the leads and the dsDNA, with $n_{L} = 1$ and $n_{R} = N$. $H_{\text{so}}$ and $H_{d}$ are, respectively, the Hamiltonians of the SOC term and the dephasing term, which will be discussed in the following.

When a charge is moving under an electrostatic potential $V$, an SOC arises $H_{\text{so}} = \frac{\hbar}{4m_{e}c} \nabla V \cdot (\hat{r} \times \hat{p})$, with the electron mass $m_{e}$, the speed of light $c$, the Pauli matrices $\sigma = (\sigma_{x}, \sigma_{y}, \sigma_{z})$, and the momentum operator $\hat{p}$. In the dsDNA, the differences of the potential are especially large between the interior and the exterior of the dsDNA, $dV/dr$ is very large at the boundary $r = R$ with $R$ the radius [19]. Hence, it is reasonable to consider the $r$-component of $V$ only and the SOC can be simplified in the cylindrical coordinate system $H_{\text{so}} = -\frac{\hbar}{4c} \sigma \cdot (\hat{r} \times \hat{p})$ with $\alpha = \frac{\hbar}{4m_{e}c} \frac{dV}{dr}$. Considering a charge propagating in one helical chain of the dsDNA (e.g., the dotted line in Fig. 1), the momentum $\hat{p} = \hat{p}_{l} \hat{l}_{||}$ with $\hat{l}_{||}$ the unit vector along the helical chain direction. Thus $H_{\text{so}}$ is reduced to $H_{\text{so}} = -\frac{\hbar}{2c} (\sigma_{x} \hat{p}_{l} + \sigma_{z} \hat{p}_{l})$.
FIG. 1: (color online). Schematic view of the dsDNA with radius $R$, pitch $h$, helix angle $\theta$, and arc length $l_a$. The circles represent the nucleobases, where the full ones assemble one helical chain and the open ones form the other helical chain. The arc length satisfies $l_a \cos \theta = R \Delta \varphi$ and $l_a \sin \theta = \Delta h$, with $\Delta \varphi$ and $\Delta h$ being the twist angle and the stacking distance between neighboring base pairs, respectively. We set $R = 1$ nm, $\Delta h = 0.34$ nm, and $\Delta \varphi = \frac{\pi}{5}$, which are typical values of B-form DNA. The circles and the helix angle and $\theta$ are rigid and the longest DNA in experiment is short [11].

The intrachain SOC is written as [25]:

$$H_{ss} = \sum_{m,s} \varepsilon_{ms}^q \Sigma_{qs,ms}^{-1} - i \Gamma_m \Sigma_{qs}^+ - \sum_{qs} \Sigma_{qs}^t \Sigma_{qs}^t \Sigma_{qs}^t \Sigma_{qs}^{-1}$$

where $\sigma^{(1)}_\perp = \sigma_x \sin \varphi \sin \theta - \sigma_y \cos \varphi \sin \theta + \sigma_z \cos \theta$ with $\theta$ the helix angle and $\varphi$ the cylindrical coordinate. Since the dsDNA consists of two helical chains, the total SOC is $\Sigma_{qs,ms} = \sum_{j=1}^2 \Sigma_{qs}^j + \Sigma_{qs}^R$. The interchain SOC has been neglected because it is very small due to the potential symmetry. By using the second quantization [21], $\Sigma_{qs,ms}$ can be written as:

$$\Sigma_{qs,ms} = \sum_{j,n} \hbar \Sigma_{qs}^j c_{jn}^\dagger (\sigma_{jn}^{(j)} + \sigma_{jn+1}^{(j)}) c_{jn+1} + H.c.,$$

where $t_{so} = -\frac{\hbar}{2m} \sigma_{n+1}^{(1)} = \Delta \varphi$, and $\sigma_{n+1}^{(1)} = \sigma_{n}^{(1)} (n \Delta \varphi + \pi)$. $l_a$ and $\Delta \varphi$ are, respectively, the arc length and the twist angle between successive base pairs.

On the other hand, a charge transmitting through the dsDNA will experience inelastic scattering from the phonons due to the fluctuation of each nucleobase around its equilibrium position and other inelastic collisions with the absorbed counterions in the dsDNA due to the negatively charged sugar-phosphate backbones [21]. Such inelastic scattering will give rise to the loss of the phase and spin memory of the charge. To simulate the phase-breaking process, Büttiker’s virtual lead is introduced by connecting to each nucleobase [22, 23], with the Hamiltonian of the dephasing term being:

$$H_d = \sum_{j,n,k} (\varepsilon_{jn} a_{jn}^\dagger a_{jn} + t_d a_{jn}^\dagger c_{jn} + H.c.)$$

$a_{jn}^\dagger = (a_{jn,1}^\dagger, a_{jn,2}^\dagger)$ is the creation operator of the virtual lead and $t_d$ is the coupling between the nucleobase and the virtual lead.

Let us demonstrate analytically that the ssDNA could not behave as a spin filter. In continuous real-space spectrum, the Hamiltonian of the ssDNA containing the SOC term is written as $H_{ss} = \frac{\hbar^2}{2m} \sigma_{n+1}^{(1)} + \frac{\hbar^2}{2m} [\sigma_{n+1}^{(j)} + \tilde{p}_j \sigma_{n+1}^{(j)}] + V(l)$ with $V(l)$ the potential energy of the helical chain. By taking a unitary transformation with the operator $U(l) = e^{i(m\alpha/h^2) \int \sigma_{nd} dl}$ [24], $H_{ss}$ is transformed into $H'_{ss} = U^\dagger H_{ss} U = \frac{\hbar^2}{2m} - \frac{m^2 \alpha^2}{2h^2} + V(l)$, which is independent of spin. Therefore, no spin polarization could be observed in the ssDNA, regardless of the SOC term, the existence of the dephasing, and other model parameters.

This result can be obtained also by using the discrete Hamiltonians of Eqs. (1) and (2). Similarly, we can also verify that any kind of SOC could not give rise to spin polarization in the ssDNA.

According to the Landauer-Büttiker (LB) formula, the current in the qth lead (real or virtual) with spin $s$ can be written as [23]:

$$I_{qs} = \langle e^2 / h \rangle \sum_{m,s} T_{qs,ms} \langle V_m - V_q \rangle$$

where $V_q$ is the voltage in the qth lead and $T_{qs,ms} = Tr [\Gamma^q q \hat{G}^t \Gamma^m \sigma_s]$, which is the transmission coefficient from the $m$th lead with spin $s'$ to the qth lead with spin $s$. The Green function $\hat{G}^t = [\hat{G}^t]^\dagger = [\hat{E} - \hat{H}_{DNA} - \hat{H}_{so} - \sum_{qs} \Sigma_{qs}^{-1}]^{-1}$ and $\hat{I}_{qs} = i \Sigma_{qs}^t \Sigma_{qs}^t$, with $E$ the incident electron energy (or the Fermi energy). $\Sigma_{qs}$ is the retarded self-energy due to the coupling to the qth lead. For the real left/right lead, $\Sigma_{L/R,s} = -i \Gamma_{L/R} / 2 = -i \pi \rho_{L/R} t_{so}^2 / 2$; while for the virtual leads, $\Sigma_{qs} = -i \Gamma / 2 = -i \pi \rho d t_{so}^2$, with the dephasing parameter $\Gamma$ and $\rho_{L/R}$ being the density of state of the leads. Since the net currents through the virtual leads are zero, their voltages can be calculated from the LB formula by applying an external bias $V_b$ between the left and right leads with $V_l = V_b$ and $V_R = 0$. Finally, the conductance for spin-up ($G^t_\uparrow$) and spin-down ($G^t_\downarrow$) electrons can be obtained

$$G^t_\uparrow = \langle e^2 / h \rangle \sum_{m,s} T_{R,s}^\uparrow \sigma_s V_m / V_b, \text{ and the spin polarization is } P^\dagger = (G^t_\uparrow - G^t_\downarrow) / (G^t_\uparrow + G^t_\downarrow).$$

For the dsDNA, $\varepsilon_{jn}$ is set to $\varepsilon_{1n} = 0$ and $\varepsilon_{2n} = 0.3$, $t_{1n}$ is taken as $t_{1n} = 0.12$ and $t_{2n} = -0.1$, and $\lambda_n = -0.3$. All these parameters are extracted from first-principles calculations [26, 27] and the unit is eV. The helix angle and the twist angle are set to $\theta = 0.5$ rad and $\Delta \varphi = \frac{\pi}{5}$, which are typical values of B-form DNA. The SOC is estimated to $t_{so} = 0.01$, which is an order of magnitude smaller than the intrachain hopping integral. In fact, all the results are qualitatively same even for smaller $t_{so}$.

For the real leads, the parameters $\Gamma_L = \Gamma_R = 1$ are fixed. For the virtual leads, the dephasing strength is very small with $\Gamma = 0.005$, because the monolayers of the dsDNA are rigid and the longest DNA in experiment is short [11].

For this value of $\Gamma$, the phase coherence length is longer than the dsDNA and the electron transport through the dsDNA will keep its phase coherence [22]. However, the
finite dephasing is indispensable. The values of all aforementioned parameters will be used throughout the Letter except for specific indication in the figure.

Figure 2(a) shows the conductances $G_{\uparrow/\downarrow}$ and the corresponding spin polarization $P_s$. One notices two transmission bands—the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO)—in the energy spectrum, where several transmission peaks are found for both spin-up and spin-down electrons (holes) due to the coherence of the system. For the HOMO band, $G_\uparrow$ and $G_\downarrow$ are almost identical, while for the LUMO band, $G_\uparrow$ and $G_\downarrow$ are very different. A bell-shaped configuration is observed in the curve of the HOMO band, $E$ vs energy $P_s$ due to the coherence of the system. For the LUMO band, $G_\uparrow$ and $G_\downarrow$ are almost identical, while for the LUMO band, $G_\uparrow$ and $G_\downarrow$ are very different. A bell-shaped configuration is observed in the curve of the HOMO band, $E$ vs energy $P_s$, where the spin polarization of the dsDNA at $N = 30$ can achieve 0.45, which is comparable with the experimental results.

To explore the physical scenario to high spin polarization observed in the dsDNA, Figs. 2(b) and 2(c) plot the conductance $G_\uparrow$ and $P_s$ in the absence of the dephasing ($\Gamma = 0$) and of the helical symmetry ($\theta = \pi$), respectively. It clearly appears that the spin polarization vanishes when $\Gamma = 0$ or $\theta = \pi$, although the conductance is still very robust in both cases. When $\Gamma = 0$, the dsDNA decouples with the virtual leads and the charge transport through the dsDNA is completely coherent. In this case, the SOC can not generate any spin polarization due to the time-reversal symmetry, the helical symmetry, and the SOC can not generate any spin polarization due to the high spin polarization. Indeed, it is reasonable to assume a small $\Gamma$ because the dephasing occurs inevitably in the experiment. On the other hand, the spin polarization strongly depends on the DNA helix. If there is no helix ($\theta = \pi$), no spin polarization could be observed ($P_s = 0$). If the right-handed helical dsDNA is transformed into the left-handed one (Z-form DNA) with $\theta \rightarrow \pi - \theta$, $P_s(\pi - \theta) = -P_s(\theta)$ exactly.

We then focus on the spin polarization $P_s$ and the averaged one $\langle P_s \rangle$, where $\langle P_s \rangle \equiv \langle (G_{\uparrow} - (G_{\downarrow})/((G_{\uparrow}) + (G_{\downarrow})) \rangle$ with $G_{\downarrow}$ averaged over the LUMO band. Figures 3(a) and 3(b) show $P_s$ at a fixed energy $E$ and $\langle P_s \rangle$ vs length $N$, respectively, for several values of the dephasing parameter. One notices that $P_s$ and $\langle P_s \rangle$ are enhanced by increasing or $\Gamma$, $N_c$ shrinks monotonically [Fig. 3(d)]. The behavior of $N_c$ vs $\Gamma$ can be fitted well by a simple function $N_c \propto \Gamma^{-1}$. For relatively large $\Gamma$ (diamond and triangle symbols), $P_s$ and $\langle P_s \rangle$ increase faster in the beginning and saturate at shorter length with smaller values because the device is more open. While for smaller $\Gamma$, $P_s$ and $\langle P_s \rangle$ increase slower with increasing $N$ in a wider range of $N$ and have larger saturation values. Let’s see $\Gamma = 0.0004$ for instance (circle symbols). $P_s$ and $\langle P_s \rangle$ will keep rising even for $N > 100$, and $P_s = 0.34$ at $N = 40$ and $P_s = 0.5$ at $N = 80$. These results are quantitatively consistent with the experiment.

In fact, the dephasing has two effects: (i) it promotes the openness of the two-terminal device and produces the spin polarization; (ii) it makes the charge lose its phase and spin memories and then $P_s$ is decreased by further increasing $\Gamma$. Accordingly, for large $\Gamma$ with the phase coherence length $L_\phi$ shorter than the dsDNA length, $P_s$ will be quite small. $P_s < 0.05$ for $\Gamma = 0.5$ and $P_s \rightarrow 0$ if $\Gamma \rightarrow \infty$. Due to the interplay between the above two effects, a small $\Gamma$, ranging from 0.0002 to 0.01, where $L_\phi$ is much larger than 100, is optimal for large $P_s$. In addition, Fig. 3(c) shows the averaged conductance $\langle G_{\uparrow} \rangle$ vs $\Gamma$. $\langle G_{\uparrow} \rangle$ is declined by increasing $\Gamma$, because large $\Gamma$ or $\Gamma$ will enhance the scattering. However, $\langle G_{\uparrow} \rangle$ remains quite large for $\Gamma = 0$ and $\Gamma = 0.012$. Therefore, the dsDNA is a well spin filter due to the large $P_s$ and $\langle G_{\uparrow} \rangle$.

Let us further study the spin polarization by varying other model parameters. Figures 4(a) and 4(b) show $P_s$ at $E = 0.488$ with $N = 80$ and $\langle P_s \rangle$ with $N = 30$, respectively, as functions of the SOC $t_{so}$ and the dephasing strength $\Gamma$. $P_s$ and $\langle P_s \rangle$ are zero exactly when $\Gamma = 0$ or $t_{so} = 0$. Of course, $t_{so}$ is a key factor for the spin polarization or equivalently $t_{so}$ is “the driving force” of $P_s$. If there is no SOC, no spin polarization would appear for whatever other parameters are. In general, strong SOC usually lead to large $P_s$ [Fig. 4(b)]. However, for a fixed energy, $P_s$ will not increase monotonically with $t_{so}$, as seen in Fig. 4(a). A large $P_s$ can be obtained for long dsDNA even for quite small $t_{so}$, because the spin polarized electrons will accumulate gradually when electrons are
transmitting along the dsDNA. In addition, we observe a large area with red color in Fig. 4(b), where $\langle P_s \rangle$ exceeds 0.1 for short dsDNA. This implies that the dsDNA would be an efficient spin filter in a wide parameters range.

Figure 4(c) plots the averaged spin polarization $\langle P_s \rangle$ vs $\Gamma$ and $\frac{\theta}{\pi}$ by fixing the radius $R$ and the arc length $l_a$ to account for the rigid sugar-phosphate backbones. The helix angle $\theta$ can be changed by stretching the DNA molecule \[29\]. It is obvious that $\langle P_s \rangle$ is zero in the absence of the helical symmetry ($\theta = \frac{\pi}{2}$) and $\langle P_s \rangle$ is increased monotonically by decreasing $\theta$. This indicates that the helix of the dsDNA plays a vital role to the existence of the spin polarization. Finally, we present the influence of the hopping integrals $t_1$ and $t_2$ on the spin polarization, as illustrated in Fig. 4(d). We can see that $\langle P_s \rangle$ is small when $t_1$ and $t_2$ have identical sign and become large when $t_1$ and $t_2$ have opposite sign. Since the sign of the hopping integral is sensitive to the type of neighboring nucleobases \[27\] and to the twist angle $\Delta \varphi$ \[31\], the spin polarization could be improved by synthesizing specific DNA molecule and putting force along the helix axis of the dsDNA.

In summary, we propose a model Hamiltonian to simulate the quantum spin transport through the dsDNA. This two-terminal dsDNA-based device would exhibit high spin polarization by considering the SOC, the dephasing, and the helical symmetry, although no spin polarization exists in the ssDNA. The spin polarization increases with increasing the DNA length. Additionally, the spin polarization could be improved by properly modifying the hopping integral and decreasing the helix angle.

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