Spin-dependent charge transport in organic semiconductors

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Abstract. Combining the Su-Schrieffer-Heeger (SSH) model and the non-equilibrium Green’s function (NEGF) formalism, we have theoretically studied controllable conductance switching of the organic spintronics and interpreted it with the voltage-induced polaron picture. The exponential decay of magnetoresistance with bias voltage is qualitatively consistent with the experimental result.

1. INTRODUCTION
The π-conjugated organic semiconductors (OSEs) have been used in the area of information display and large-area electronics owing to their ability to be economically processed in large areas, their compatibility with low-temperature processing, the tunability of their electronic properties, and the simplicity of thin-film device fabrication[1]. Recent successes in the field of molecular electronics on the electrical properties of OSE nano-structures between two metal electrodes have revealed many unique charge transport phenomena, such as negative differential resistance (NDR)[2] and bistable switching[3], etc. Though some applications of these unique properties have been reported[4], no persuasive mechanisms are available at present. On the other hand, the OSEs have extremely weak spin-orbital interaction and weak hyperfine interaction, so that electron spin diffusion length is especially long[5], which make them ideal for spin-polarized electron injection and transport applications in the new field of spintronics. Recently, a giant negative magnetoresistance as large as 40% has been detected[6] in an organic spin-valve structure LSMO/OSE/Co.

In this paper, we devote to the above issue by investigating the spin-dependent charge transport properties in the organic spintronics devices with the Su-Schrieffer-Heeger (SSH) model combined the non-equilibrium Green’s function (NEGF) formalism. we focus our study on the bistable switching.

Bistable switching means a controllable hysteretic (bistable) current characteristic with the linear sweeps of the bias voltage in the solid state condition[7] or of the potential of the electrodes in the electrochemical condition[8]. Switching between two conductance (high and low) states of molecules in a sealed nanopore system has been used for molecule-based memory devices[4].
Recent experiment has demonstrated that, distinctly different from the voltage-independent stochastic switching, voltage triggered switching is indeed a molecular phenomenon [9].

2. Model and Calculation

In the study of the electronic conductivity and optical phenomena in π conjugated OSEs, SSH model [10] has been shown a remarkable track of success. In addition to the polyacetylene, it has been applied to molecular systems [11], carbon nanotubes [12] and DNA molecule [13]. The SSH model captures the essential characteristic of the conjugated organic materials, i.e., the strong e-ph coupling which leads to the dimerized ground state and polaron (or soliton) charged states.

Since currently used OSEs for spintronics typically have a nondegenerate ground state [14], we use a nondegenerate version of the one-dimensional (1D) SSH model to describe them,

\[
H_O = \sum_{n,\sigma} \left( \epsilon_o c_{n,\sigma}^+ c_{n,\sigma} - \left[ t_o - t_1(-1)^n - \alpha_o (u_{n+1} - u_n) \right] (c_{n,\sigma}^+ c_{n+1,\sigma} + \text{H.c.}) + \frac{K_o}{2} (u_{n+1} - u_n)^2 \right) \quad (1)
\]

Here, \(\epsilon_o\) is the on-site energy of an atom or an unit renormalized to one site in the tight-binding scheme; \(c_{n,\sigma}^+ (c_{n,\sigma})\) denotes the creation (annihilation) operator of an electron at the nth site with spin \(\sigma\), while \(u_n\) stands for the displacement of the site from its equilibrium position; \(t_o\) is the zero-displacement hopping integral, \(\alpha_o\) the electron-phonon coupling, \(K_o\) the spring constant, and \(t_1\) introduces nondegeneracy into the OSE structure.

In the present work, we choose symmetrical ferrimagnetic (FM) 3d transition metals as electrodes. The spin-dependent charge transport mainly takes place between their 3d bands. Neglecting the spin-flip during transport and adopting the two current model [15], we describe the FM metal by 1D single d band tight-binding model with a spin splitting term [16],

\[
H_F = \sum_{n,\sigma} \left( \epsilon_f c_{n,\sigma}^+ c_{n,\sigma} + t_f (c_{n,\sigma}^+ c_{n+1,\sigma} + \text{H.c.}) \right) - \sum_n J_f (c_{n,\uparrow}^+ c_{n,\downarrow} - c_{n,\downarrow}^+ c_{n,\uparrow}), \quad (2)
\]

where \(\epsilon_f\) is the on-site energy of a metal atom, \(t_f\) is the nearest neighbor transfer integral, and \(J_f\) is the Stoner-like exchange integral.

The non-equilibrium Green’s function (NEGF) approach based on the Keldysh formalism [17, 18] is used to calculate the quantum transport properties of organic spintronics. To do that, the spintronic devices are divided into three distinct regions: two semi-infinite ferromagnetic electrodes (L and R) and a central scattering region where the OSE is located. The leads, acting as charge reservoirs, set the temperature and electronic distribution of the metals in the steady state. With the self-energy scheme, we can reduce the infinite non-periodic open system to that of calculating the Green’s function of the central scattering region.

Using the SSH model for OSE and 1D tight-binding model for electrodes, we can construct the retarded Green’s function \(G(E)\) of the scattering region in the presence of the leads as

\[
G(E) = (E - H_S - \Sigma_L - \Sigma_R)^{-1}.
\]

\(H_S \equiv H_L + H_O + H_R + H_I\) denotes the Hamiltonian of the scattering S-region, which consists of the coupled OSE and some metal atoms at the lead interfaces. The bulk leads serve as electron reservoirs and contribute to the self-energy matrices \(\Sigma_L\) and \(\Sigma_R\). The broadening matrix \(\Gamma_L/R\) is defined as \(\Gamma_L/R = i \left( \Sigma_L/R - \Sigma_L^I/R \right)\).

One can then evaluate the density matrix as

\[
\rho = \frac{1}{2\pi} \int_{-\infty}^{\infty} \left[ f(E, \mu_L) G_L G_I^\dagger + f(E, \mu_R) G_R G_I^\dagger \right] dE, \quad (3)
\]

and the total number of electrons is \(N = \text{Tr} (\rho S)\). In Eq. (3) \(f(E, \mu_{L/R})\) is the Fermi distribution
function at the chemical potentials of the leads $\mu_L/R$. The current is given by \[ I = \frac{2e}{h} \int_{-\infty}^{\infty} \text{Tr} \left( \Gamma_L G \Gamma_R G^\dagger \right) \left[ f(E,\mu_L) - f(E,\mu_R) \right] dE, \] (4)

with $\text{Tr} \left( \Gamma_L G \Gamma_R G^\dagger \right) = T(E,V)$ being the transmission coefficient function.

The integrand in Eq. (3) can be divided into the equilibrium density matrix part and the bias induced part. They can then be evaluated by contour integration and direct multi-grid Gaussian integration, respectively. Numerical implementation will be carried out in a real-function basis set representation, and the resulting density matrix $\rho$ will be real [18].

We adopt an efficient numerical arithmetic through solving the quadratic eigenvalue equation to achieve the self-energy [20]. Though the analytical solution of the one-dimensional FM metal is possible, the numerical approach present in this work can be easily extended to study the magneto-transport beyond the one-dimensional system.

We assume the bias $V$ does not change the electronic structure of the L and R leads, but shifts their energy levels by $V/2$ and $-V/2$, respectively. In contrast to the leads, due to the presence of the potential drop, the effects of electric bias on OSE need to be calculated by solving the Poisson’s equation with the method of images,

$$\nabla^2 V_H(x) = - \sum_{n=1}^{N_S} \frac{q_n}{\varepsilon_0} \delta(x_n - x),$$

(5)

together with the boundary conditions of $V_H(x_1) = V/2$ and $V_H(x_{N_S}) = -V/2$. We describe the electron-wavefunction-dependent lattice distortion via the Hellman-Feynman theorem,

$$0 = \frac{\partial E_S}{\partial u_n} = 2\alpha_S (\rho_{n,n-1} - \rho_{n+1,n}) + K_S (y_n - y_{n+1}).$$

(6)

$E_S = \text{Tr} \left[ \rho H_S \right]$ denotes the electronic energy of the extended OSE system, and $y_n = u_n - u_{n-1}$. The Hellman-Feynman theorem states that the static lattice distortion should be evaluated from the non-equilibrium density matrix.

3. Results and Discussion

Depending on the magnetization direction, there are two possible configurations of the FM electrodes, parallel($P$) or antiparallel($AP$) aligning with respect to each other. In the $P$ configuration, the down-spin electrons of $L$ can transport to $R$ through the spin-degenerate OSE under bias but the up-spin electrons can not due to its completely filled band. The current dependence of the linear bias sweeps at the parallel alignment is shown in Fig. 1, where the up and down sweeping direction of the bias are indicated by the arrows.

Below $\sim 1.5$ V, the OSE is in the insulating state and the current is near zero(< 0.5 nA). Increasing the potential to $\sim 1.5$ V, the current jumps suddenly by more than one orders of magnitude to $\sim 8$ nA. Then the current almost keep unchanging with the increase of bias until at $\sim 2.8$ V the second switching happens where the current abrupt increase to $\sim 45$ nA. Although the OSE can be reversibly switched between conducting and insulating states, two large hysteresis are apparent, one is from 0.5 V to 2.0 V and the other from 2.0 V to 3.0 V. The two-step switching process has been found in a polymer nanojunction switch[8] when it is shorten to several nanometers, in the same length scale as in our theoretical work.

We believe voltage-controlled conductance switching is due to the charge variation induced by bias voltage. In the insert of Fig. 3, we plot the charge changing($\Delta q_o$) induced by the
sweeping bias with respect to the total charges within OSE sub-structure under the equilibrium condition. A synchronous dependence of $I$ and $\Delta q_o$ with the bias sweeps is clearly shown. Since the wavefunctions are significantly delocalized from the OSE sub-structure into the metal leads, the number of electrons in the OSE can change by fractional amounts. Adding or moving electrons from the OSE sub-structure is known to form polaron(or bipolaron) charged states because of the strong e-ph coupling.

Besides the bias-dependent conductance switching, another type of conductance switching controlled by the sweeping of the electrodes potential in the electrochemical condition has been reported[8]. In Fig. 3, we give the dependence of charge transport current on the sweeping of electrochemical potential $E_P$(vs. the initial Fermi level of metal leads $E_F$) for the parallel configuration together with the charge changing within OSE sub-structure induced by the sweeping potential. The bias voltage between the electrodes is kept at 20 mV. With the increase of potential, the current undergoes a rapid increase starting from about 0.5 V and reaching a maximum near 0.8 V, as the OSE is switched from insulating to conducting state. The hysteresis behavior is attributed to the formation of polarons carrying about two localized electrons, as shown in the insert of Fig. 3. The electrochemical potential-dependent charge transport behavior is similar to the bias voltage-dependent behavior since both of them induced from the same physics mechanism, that is, the polaron assistant charge transport. Similar dependence of charge transport current on the sweeping of $E_P$ has been found for the antiparallel configuration.

We then calculate the current through OSE spintronics at the conducting state as a function of the bias voltage both for the parallel and antiparallel configuration(Fig. 4). The current for the parallel configuration is found roughly linear as expected for a metallic phase, but that of the antiparallel increases much slower after a small voltage gap about 0.05 V. The asynchronous change of current with the bias voltage may induce large magnetoresistance which is defined as, $MR = \frac{\Delta R}{R} = \frac{R_{AP} - R_P}{R_{AP}}$ where $R_{AP}$ and $R_P$ are the resistance in the antiparallel and parallel states. The dependence of MR on the bias voltage is shown in the insert of Fig. 4. In our ideal system where spin flipping totally ignored, much larger MR value is found than those reported in the experiments up to now, especially at bias voltage $V \approx 0$, MR almost reaches 100%. From $V = 0$ to 0.5 V, MR decays exponentially with the increase of bias voltage. As shown in Fig. 4, $R_P$ almost keeps a constant under the low bias voltage($\approx 17 \text{ M}\Omega$), therefore the
Figure 3. Charge transport current vs sweeping of electrochemical potential for the parallel configuration. The insert is the charge changing within OSE sub-structure induced by the sweeping potential.

Figure 4. I-V characteristics of the OSE spintronics at the conducting state both for the parallel(solid line) and antiparallel configuration(dashed line). The insert is the MR as a function of the bias voltage.

$R_{AP} - V$ behavior dominates the voltage dependence of MR. In the AP configuration, during the electrons transports from the polaron level of OSE to the peak in the minority spin DOS, the $R_{AP}$ progressively decreases from a infinite large value to a smaller finite one with the increase of the bias voltage, and consequently causes the exponential decay of MR. The exponential decay of MR with the bias voltage has been reported in the recent experiments, where the MR is also found peaking at $V \approx 0$ and decreasing as the applied voltage increases[6]. The exponential decay of MR with the bias voltage in organic spintronics is similar to what was observed in magnetic tunnel junctions with LSMO and Co or CoFe electrodes[21, 22].

4. Summary
In summary, with the SSH model combined NEGF formalism, we have investigated the spin-dependent charge transport in the organic spintronics controlled by bias voltage or electrodes potential. The conductance switching is proved to result from the formation of polarons in the organic sub-structure. The magnetoresistance is found exponential decaying with bias voltage, which is qualitatively consistent with the recent experiment.

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