Magnetoresistance in organic spintronic devices: the role of nonlinear effects

A V Shumilin¹, V V Kabanov² and V A Dediu³

¹ A.F.Ioffe Physico-Technical Institute, St.-Petersburg 19 4021, Russia
² Department for Complex Matter, Jozef Stefan Institute, 1001 Ljubljana, Slovenia
³ CNR—ISMN, Consiglio Nazionale delle Ricerche—Istituto per lo Studio dei Materiali Nanostrutturati, v. Gobetti 101, 40129, Bologna, Italy

E-mail: viktor.kabanov@ijs.si

Abstract

We derive kinetic equations describing injection and transport of spin-polarized carriers in organic semiconductors with hopping conductivity via an impurity level. The model predicts a strongly voltage dependent magnetoresistance, defined as resistance variation between devices with parallel and antiparallel electrode magnetizations (spin-valve effect). The voltage dependence of the magnetoresistance splits into three distinct regimes. The first regime matches well-known inorganic spintronic regimes, corresponding to barrier-controlled spin injection or the well-known conductivity mismatch case. The second regime at intermediate voltages corresponds to strongly suppressed magnetoresistance. The third regime develops at higher voltages and accounts for a novel paradigm. It is promoted by the strong nonlinearity in the charge transport whose strength is characterized by the dimensionless parameter $eU/k_B T$. This nonlinearity, depending on device conditions, can lead to both significant enhancement or to exponential suppression of the spin-valve effect in organic devices. We believe that these predictions are valid beyond the case of organic semiconductors and should be considered for any material characterized by strongly nonlinear charge transport.

1. Introduction

Magnetoresistance in organic spintronic devices is an easy effect to detect [1]. Vertical, multilayered devices combining manganite ($\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$) and cobalt external magnetic electrodes with an $\text{Alq}_3$ transport interlayer have perhaps never failed (no negative reports are available) to exhibit a clearly measurable magnetoresistance [2–6]. This magnetoresistance, often called in the literature giant magnetoresistance (GMR) or the spin-valve effect (SV), is generally measured as a difference between the device resistances for antiparallel and parallel electrode magnetizations, where the latter is expected to facilitate the transport of spin-polarized currents. Manganite-based devices commonly show an inverse spin-valve effect featuring lower resistance for antiparallel orientation. This property was explained recently by the spin-filtering effects at the organic–ferromagnetic interface [7–9]. Substituting the manganite with a three-dimensional metal or other magnetic electrode leads to a more controversial picture that merges successes and failures. Generally, this second case has well-established achievements in the tunneling regime, that is, for a few nm thick layer of various organic semiconductors [10, 11]. On the other hand, the application of two metallic magnetic electrodes in combination to thick organic layers, expected to transport carriers via molecular electronic states, has led to a number of reports claiming no magnetoresistance (see, for example, [12] and high thicknesses regimes in [10, 11]) and a number of positive communications [13, 14].

An important fact to underline is the voltage dependence of the GMR in organic-based devices. The magnetoresistance is generally detectable at relatively small voltages ($\leq 0.1$ V), which are much lower than interfacial electronic barriers for the injection into two-transport states of organic semiconductors (OSC), highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO). Indeed,
typical values of the barriers measured by various spectroscopic techniques are of the order of 1 eV [5]. This clearly implies the need to consider eventual intragap states or bands, as discussed in [15, 16]. It is also known from experiments that impurity states can be created in OSC in an uncontrollable way during sample preparation [17].

Such easily achievable spintronic effects in electrically operated organic devices looked strange, especially when compared to their inorganic counterparts, where the fight with materials and concepts impeded similar achievements for years of tough and extremely qualified research. For inorganic devices these difficulties were convincingly explained through the conductivity mismatch problem [18–20]. A fundamental obstacle for the spin injection from a ferromagnetic metal to a semiconductor was formulated by Schmidt et al. [18]. It was shown that in the case of diffusive transport, the large difference in conductivities of a ferromagnetic metal and semiconductor limits the spin injection coefficient $γ \propto \sigma_f/\sigma_s$, where $\sigma_f$, $\sigma_s$ are conductivities of a semiconductor and ferromagnetic metal, respectively. This limitation can be overcome by introducing a tunneling barrier at the ferromagnetic–semiconductor interface [20, 22], leading to an essential improvement of the spin injection into a semiconductor. In order to be effective, the tunnel resistance should be of the order of the effective resistance defined as $L_s/\sigma_s$, $L_f/\sigma_f$, where $L_s$, $L_f$ are the spin diffusion lengths in ferromagnetic metal and semiconductors, respectively.

The question of whether OSC are free of conductivity mismatches, or if the MR in OSC might not be caused by real spin injection into the organic electronic states has been raised. The latter doubt was strongly enhanced by the absence of the Hanle effect in all the tested organic spintronic devices [23, 24]. Indeed, a device based on the transport of spin-polarized carriers, the application of a magnetic field perpendicular to the carrier’s spin causes the latter to precess with a frequency 28 GHz per Tesla, regardless of whether the transporting medium is inorganic or organic. This precession causes a misalignment between the relative orientation of the injected spin polarization and the electrodes’ magnetization, resulting in a measurable resistance change. It is noteworthy that in inorganic spintronics the Hanle effect has acquired the role of offering decisive proof for the demonstration of a spin-polarized electrical injection in the investigated medium [25, 26].

While interesting and stimulating ideas have already been advanced to explain the absence of the Hanle observation [27], we would like to underline an important paradox related to organic spintronic devices. Although magnetoresistance represents the parameter whose variation is used to indicate the strength of the Hanle effect, the nature of magnetoresistance in such devices is not clearly understood.

Currently, there have been few attempts to model spin transport in organic semiconductors [7, 28, 29]. The first successful approaches to describe magnetoresistance in OSC were based on the extension of the models describing inorganic devices [20, 22] through an accurate inclusion of the mechanisms of charge injection in OSC [28]. An important step forward was proposed in [29, 30]. The authors have considered a model of multistep tunneling through a single molecular level in OSC and the finite occupation of the level during the tunneling process. Thus, for the first time it promoted elements of nonlinearity for the spin-polarized carrier transport inside OSC. Nevertheless, nonlinear effects were considered only for a small number of intermediate states, while for the bulk hopping case, the resistance of organic was described as a constant [29].

Here, we make a step further and consider charge transport nonlinearity in an organic semiconductor confined between two spin-polarized electrodes. We limit our model to the conductivity via a single intragap electronic level. In spite of its obvious simplification (compared to strongly nonhomogeneous situation in OSC), the model clearly confirms the two well-known spintronic regimes described above, and namely, the conductivity mismatch [18] and the tunnel barrier regime [20, 22], as expected from both experimental results and theoretical predictions. Surprisingly, we discover a third regime, explicitly characteristic of organic semiconductors, where nonlinear effects induce a measurable magnetoresistance. Indeed, for strongly voltage-dependent hopping transport through the molecular level, the conductivity becomes strongly dependent on the injected spin. We demonstrate that in a high voltage limit $eU/k_B T \gg 1$, the resistance of the organic semiconductor is governed by the contacts. Here, $e$ is the elementary charge, $U$ is the voltage, $k_B$ is the Boltzmann constant, and $T$ is the temperature. In that case, boundary conditions define the resistivity of the organic semiconductor, and therefore the resistivity becomes spin-dependent. It means that contrary to the case of an ordinary semiconductor with diffusive transport, the conductivity mismatch arguments are applicable for organic semiconductors only for some limited voltage range, while for higher voltages, strong nonlinear effects in organic semiconductors enable the detection of the magnetoresistance caused by spin-polarized injection.

Although we have formulated the model for the conductivity via the impurity level, it is valid for any energy level with hopping conductivity when the space-charge may be neglected. As a result, the model is valid if the conductivity occurs over the HOMO and LUMO, provided the concentration of the injected carriers is small. The experimental situation as far as transport in SV devices is concerned remains controversial. The transport due to electron and hole injection into the HOMO and LUMO is commonly assumed in literature [28, 31]. On the other hand, the $I$–$V$ characteristics of the device in that case should be highly nonlinear and sensitive to the temperature [16]. This has not been reported experimentally. These arguments suggest that the conductivity of the SV devices is
due to the existence of some impurity levels when the applied voltages are much less than Fermi level-LUMO (and Fermi level-HOMO) distance [15]. The origin of the impurity levels may be different (for example, metal atoms, oxygen molecules [16] or x-rays-induced traps during electron-beam deposition of metallic electrodes [17]). Contrary to [16], where it was suggested that impurity levels have wide energy distribution between the HOMO and LUMO, we assume that the impurity level has narrow energy distribution. We show in our work that for such levels, the nonlinearity can both suppress and enhance the spin-valve effect in some cases.

2. Main equations

In order to describe nonlinear effects, we assume that the transport in an organic semiconductor in the low voltage limit ($eU \ll \Delta$, $\Delta$ is the LUMO–HOMO splitting) is determined by the polaron hopping over impurity levels similar to [27]. In order to have reasonable conductivity, the level should have energy close to the Fermi energy. We assume that the density of this level’s $n$ is relatively small ($\lesssim 10^{18}$ cm$^{-3}$), and therefore we can neglect the electric field that appears due to the finite occupancy of the impurity levels by polarons. The electric field inside the semiconductor is equal to the external field in that case. We also assume that spatial energy fluctuations of these impurity levels are small $\Delta e \ll k_B T$.

To describe the polaron-hopping transport, we apply the stationary kinetic equation for the distribution function $f_\sigma(m)$ in the site representation derived in [32]:

$$0 = \sum_{m'} \left( f_\sigma(m') \left( 1 - f_\sigma(m) \right) \right) W_{m',m} - f_\sigma(m) \left( 1 - f_\sigma(m') \right) W_{m,m'}$$

(1)

where

$$W_{m,m'} = \exp \left( \beta eE(m'-m) \right) w(|m'-m|)$$

(2)

and $w(|n|) = \frac{1}{2\beta} \frac{\beta E_0}{\beta}$ $\exp (-\beta E_0)$. Here, $\beta = 1/k_B T$, $E_0$ in the activation energy of the polaron, $\hbar$ is the Planck constant, $e$ is the charge of the electron, and $J(|n|)$ is the overlap integral between the two sites. This equation is derived under the condition that spin relaxation is absent and the Hubbard energy is neglected. We consider only the case of the weak field $\beta eE_0 \ll 1$ ($a$ is the hopping distance); therefore, we can keep only the lowest order in the expansion of the hopping probability in the electric field $E$: $W_{m,m'} = w(|m'-m|)(1 + \beta eE(m'-m))$. Assuming that the distribution function $f_\sigma(m)$ is a smooth function of $m$, we could expand $f_\sigma(m') = f_\sigma(m) + (m'-m) \frac{df_\sigma}{dm'}(m) + \frac{(m'-m)^2}{2} \frac{d^2f_\sigma}{dm'^2}(m)$ and consider $m$ as a continuous variable $x$. In that case, equation (1) reads:

$$D \frac{d^2f_\sigma(x)}{dx^2} + \beta eEDf_\sigma(x) \left( 1 - f_\sigma(x) \right) = 0$$

(3)

Here, the spin-independent diffusion coefficient is defined as $D = \sum_n w(n)n^2a^2/6$. $\beta eDf_\sigma(1 - f_\sigma)$ is the local conductivity of polarons with the spin $\sigma$. The first integrals of this equation (3) define the currents of spin ‘up’ $J_\uparrow$ and spin ‘down’ $J_\downarrow$ polarons:

$$\frac{J_\uparrow}{e} = D \frac{df_\uparrow(x)}{dx} + \beta eEDf_\uparrow(x) \left( 1 - f_\uparrow(x) \right)$$

$$\frac{J_\downarrow}{e} = D \frac{df_\downarrow(x)}{dx} + \beta eEDf_\downarrow(x) \left( 1 - f_\downarrow(x) \right)$$

(4)

Here, $n$ is the density of the conducting levels. These equations are similar to ordinary diffusion equations describing spin–polarized currents in ordinary semiconductors [33, 34]. The main difference is in the dependence of the drift current on the distribution function. If the distribution function is small, the current is defined by $f \ll 1$. If the level is filled by electrons, the current is determined by the concentration of holes $(1 - f)$. The later term is missing in the ordinary description of the spin transport in semiconductors described by an ordinary diffusion equation. These equations do not include the spin-relaxation term (its effect will be discussed below). This holds if the thickness of the organic layer $L < \sqrt{D\tau}$, where $\tau_s$ is the spin–relaxation time in an organic semiconductor. In the case of an organic semiconductor $\tau_s \approx 10^{-3} - 10^{-6}$ s [35] is large and $\sqrt{D\tau}$ is of the order of few hundred nanometers.

Equation (4) should be supplied by the boundary conditions, which describe the microscopic structure of the contacts. Here, we consider an oversimplified model (similar to that proposed in [22]) that assumes the absence of the spin relaxation in the contacts. The change of electrochemical potential $\delta \xi$ in the contact is approximate by Ohm’s law $\delta \xi_{\sigma} = f_{\sigma}R_{\sigma}$, where $\xi$ stands for right and left interface, and $\sigma = \uparrow$, $\downarrow$ stands for ‘up’ and ‘down’ spin polarization. $R_{\sigma}$ are the contact resistivities for up and down spins.
Differently from [22], in our case it is important to consider not only the change of the electrochemical potential \( \Delta \xi_{\text{L},1} \), but also the contribution to it from the contact voltage. Note that the organic side of the contact cannot have surface charge; therefore, the electric field in the contact is the same as in the bulk of the organic layer. It means that we can neglect the contact voltage provided that the contact is much shorter than the thickness of the organic layer. Therefore, the change of the electrochemical potential \( \Delta \xi_{\text{L},1} \) is equal to the change of chemical potential. This means that the boundary conditions for the distribution function at the interface are defined as follows:

\[
\begin{align*}
    f_{\text{L},1}(0) &= \exp\left(\frac{1}{\beta(E_0 - e \kappa \xi_{\text{L},1} - \kappa \xi_{\text{L},1})}\right) + 1, \\
    f_{\text{L},1}(L) &= \exp\left(\frac{1}{\beta(E_0 + e \kappa \xi_{\text{L},1} - \kappa \xi_{\text{L},1})}\right) + 1
\end{align*}
\]

Here, \( E_0 \) is the position of the energy level in an organic semiconductor with respect to the Fermi level. As a result, equation (4) define the distribution function \( f_{\text{L},1}(x) \) inside the organic layer. The substitution of this solution to the boundary conditions given in equation (5) allows us to obtain the equation for the current \( j_{\text{L},1} \).

In order to discuss the current–voltage characteristics and the spin-valve effect, we rewrite equation (4) in dimensionless form:

\[
\frac{df_{\text{L},1}(y)}{dy} + f_{\text{L},1}(y)\left(1 - f_{\text{L},1}(y)\right) = \frac{j}{nD},
\]

where dimensionless current defined as \( j_{\text{L},1} = j_{\text{L},1} L/nD \), and dimensionless voltage \( \xi = \beta eE_0, y = \alpha x, \alpha = \xi/L \).

The general solution of equation (6) is:

\[
f_{\text{L},1}(y) = \frac{1}{2} \left(f_{\text{L},1} - f_{\text{L},1}\right) \tanh\left(\beta y - \gamma_{01,1}\right).
\]

where we introduce the dimensionless position of the energy level in the organic semiconductor \( \beta E_0 = \epsilon_0 - \epsilon_n \), and the dimensionless contact resistances defined as \( r_{\text{L},1,1} = R_{\text{L},1,1}/R_o \) and the resistance of organic layer is \( R_o = L/\beta \epsilon_n nD \). Unfortunately, accurate solutions for these equations are possible only by numerical techniques. Some accurate analytical solutions are possible only in some limiting cases. The spin-valve magnetoresistance is defined as follows:

\[
MR = \frac{j_p - j_\alpha}{j_\alpha + j_p}
\]

where \( j_{\alpha,p} \) is the current of the device with parallel and antiparallel polarization of the ferromagnetic electrodes with the fixed voltage. For practical purposes, it is convenient to exclude \( \exp(-\gamma_{01,1}) \) from equation (8) as a result, we obtain a single transcendental equation for the current \( j \):

\[
\left( f_{\text{L},1} - f_{\text{L},1}\right)\left(f_{\text{L},1} - f_{\text{L},1}\right) = e^{-\gamma_{01,1}}\left(f_{\text{L},1} - f_{\text{L},1}\right)\left(f_{\text{L},1} - f_{\text{L},1}\right).
\]

Here, \( \xi = \kappa \xi \).

### 3. Magnetoresistance

The results of numerical solution of equation (10) for currents and spin-valve magnetoresistance in equation (9) are plotted in figure 1. From this figure, we see that the spin-valve magnetoresistance has three characteristic regions. At small voltages \( eU \ll k_B T \), we expand in equation (10) \( f_{\text{L},R,1,1} \) up to the first order in \( r_{\text{L},1,1} \). After straightforward calculations, we find

\[
j_{\text{L},1} = \frac{\xi}{\eta_{1,1} + r_{\text{L},1,1} + r_o},
\]

where the resistance of the organic layer is defined as \( r_o = 4 \cosh^2(\epsilon_0/2) \). Therefore, in the limit of low field spin-valve magnetoresistance, \( MR \) is governed by the conductivity mismatch condition and by the contact resistances.
Indeed, in this limit we are able to reproduce well-known results for ordinary semiconductors \cite{18, 20, 22}. In the symmetric case $\sigma_{L,R} \uparrow \downarrow = \sigma_{R,L} \uparrow \downarrow$, spin-valve magnetoresistance is given by the formula:

$$MR = \frac{(\sigma_L - \sigma_R)^2}{(\sigma_L + \sigma_R + \sigma_0)^2 + (2\sigma_L + \sigma_0)(2\sigma_R + \sigma_0)}.$$  

(12)

Therefore, in the case when total resistance is governed by the resistance of the organic layer, we have $MR \ll 1$, which agrees with \cite{18, 20}. For large enough contact resistances, equation (12) gives a measurable magnetoresistance that agrees with the results of \cite{20, 22}.

The spin-valve magnetoresistance decreases with applied voltage because effective resistivity increases with $U$. In the limit of intermediate voltage $eU \gg k_B T$ ($\zeta \gg 1$), the nonlinear effects become important. The rhs of equation (10) is exponentially small $\zeta^{-\lambda}$ and can be neglected. In that case, equation (10) has two roots leading to the transcendental equations for the current:

$$f_{L,1} = f_{L,1} \Rightarrow j_{L,1} = \frac{\zeta}{\exp(-\epsilon_0 + \eta_1, j_{L,1}) + 1}$$

$$f_{R,1} = f_{R,1} \Rightarrow j_{R,1} = \frac{\zeta}{\exp(\epsilon_0 + \eta_1, j_{R,1}) + 1}$$

They have two solutions, $j_{L,1}$ and $j_{R,1}$ respectively. The correct solution should satisfy the condition $f_{L,1} > f_{L,1} > f_{R,1}$, $f_{R,1}$. These inequalities are satisfied if $j_{L,1} = \min (j_{R,1}, j_{L,1})$. This formula defines current voltage characteristic in the large-current limit.

For the intermediate field case, when $k_B T \ll eU \ll E_0$ ($1 \ll \zeta \ll \epsilon_0$), the correct root is determined by the sign of $\epsilon_0$. In this case, the conductivity is determined by the contact with positive energetic mismatch, and the device shows no evidence of the spin-valve effect. The actual value of the spin-valve magnetoresistance $MR$ is an exponentially small function of the applied voltage $\zeta^{-\lambda}$.

However, at higher voltages when $j_{R,1} \gg \epsilon_0$, the correct root is determined by the position of the organic level $\epsilon_0$, but by the largest of the contact resistances. In the antiparallel (AP) configuration the root is always defined by the resistance $r_1$. Here, we again assume that $r_1 > r_1$. On the other hand, in the parallel (P) configuration for one of spin directions the boundary with the resistance $r_1$ is absent and the root is determined by $r_1$. It leads to the reappearance of the spin-valve magnetoresistance at large voltage. In order to clarify these processes, we plot in figures 2 and 3 the spatial dependence of the level occupancy and the chemical potential in the organic level for the parallel and antiparallel configurations. As is clearly seen, the resistivity of the device is determined by the small density of holes in the left part of the organic layer and by the small density of electrons in the right part of the layer. Therefore, the resistance of the antiparallel configuration is equal to the resistance of the parallel configuration $P \uparrow$. The parallel configuration $P \downarrow$ has lower resistance, leading to a large magnetoresistance.

With a further increase of voltage, the equation for current can be solved with the logarithmic accuracy $j_{L,R,1} = \eta_{L,R,1}^{-1} \ln(\zeta)$. In this limit, the spin-valve magnetoresistance increases, logarithmically approaching the limiting value:
which is larger than weak field value (12). This formula does not contain any information about the resistance of the organic layer and therefore represents the perfect device.

We have described above three limiting cases for the spin-valve effect. It is important to note that the position of the conducting level $\epsilon_0$ with respect to the chemical potential of ferromagnetic contacts is a key parameter for establishing a magnetoresistance (spin-valve effect). Figure 4 shows the dependence of the magnetoresistance on the difference between level energy and chemical potential of the ferromagnetic layer $\epsilon_0$ for constant $r_{\uparrow, \downarrow}$ resistances. When $\epsilon_0 < 1$, the spin-valve effect monotonically grows with applied voltage reaching the asymptotic value equation (13) (Figure 4). When $\epsilon_0 = 1.5$, the minimum of spin-valve effect at intermediate values of electric fields $\zeta$. At $\epsilon_0 = 2$, we clearly see the three regions, including where the spin-valve effect is fully suppressed.

4. Spin relaxation

By neglecting the spin relaxation (as is done in [22]), it is possible to suppress conductivity mismatch only by introducing the contact resistances. When the contact resistances become larger than the resistance of the normal layer, the device is not subject of the conductivity mismatch, and a high SV effect can be achieved.

This is not the case if even a weak spin relaxation is included. It was shown in [20, 21] that large contact resistances lead to strong spin accumulation and depolarization near the boundary. So the contact resistances should be selected in a narrow range to avoid both phenomena: spin depolarization and conductivity mismatch.
Indeed, our model differs from those discussed in [20] and [22]. In our case, the conductivity mismatch is suppressed not only by the contact resistance but also due to applied voltage and nonlinearity. Also, we have some limit for spin accumulation because in our case the number of electronic states is finite and we cannot have $f_\uparrow$ or $f_\downarrow$ larger than unity.

Let us now include in our equations a spin-relaxation time $\tau$ that does not depend on applied voltage

$$D \frac{d^2 f_\sigma(x)}{dx^2} + \beta e E D \frac{df_\sigma(x)}{dx} \left( f_\sigma(x) \left( 1 - f_\sigma(x) \right) \right) = \frac{f_\sigma(x) - f_{-\sigma}(x)}{\tau}.$$  

After introducing spin currents in the dimensionless form, we obtain

$$\frac{dl_\uparrow}{dy} = -\frac{dl_\downarrow}{dy} = \frac{\gamma}{\xi} \left( f_\uparrow - f_\downarrow \right), \quad \gamma = \frac{L^2}{D\tau};$$

$$\frac{df_\uparrow}{dy} + f_\uparrow \left( 1 - f_\downarrow \right) = j_\uparrow/\xi;$$

$$\frac{df_\downarrow}{dy} + f_\downarrow \left( 1 - f_\uparrow \right) = j_\downarrow/\xi.$$  

This set of equations is much more complex than equations without spin relaxation and allows only numerical analysis. Let us also note that the perturbation theory for small $\gamma$ is not useful in our case because the correct perturbation parameter appears to be $\gamma e^\xi$ and quickly becomes large at high voltages. Therefore, we solve these equations numerically for the case $\epsilon_0 = 0$.

Figure 5 shows the numerical solution for a device with $r_\uparrow = 5$, $r_\downarrow = 1$, $\epsilon_0 = 0$ and different relaxation rates $\gamma$. The results for $\gamma = 0$ agree with the analytical solution. It can be seen that a relatively small spin relaxation of $\gamma = 0.1$ does not alter magnetoresistance significantly, even at high voltages $\zeta$. The tendency of magnetoresistance to grow with applied voltage remains even for the large relaxation rates $\gamma \geq 1$.

5. Discussion

In a fully metallic device, the conductivity of the normal layer does not depend on the shift of chemical potential. The description of the device in terms of electrochemical potential does not require knowledge of the separate contributions from electrical and chemical potentials. In our case, where the conductivity is governed by few functional levels near the Fermi level, the situation is different. Small shifts of the chemical potential drastically change the conductivity of the intermediate layer. Indeed, assuming the existence of the local chemical potential via the distribution function

$$f_\sigma = \frac{1}{\exp \left( \beta (\epsilon_0 - \mu_\sigma(x)) \right) + 1}.$$
we may rewrite equation (4) in the standard form

\[ \frac{J_\sigma}{e n} = \sigma(\mu) \frac{d\xi_\sigma}{dx}, \]

where \( \xi_\sigma \) is electrochemical potential and \( \sigma(\mu) = \beta e D f_\sigma(1 - f_\sigma) \) is chemical potential dependent conductivity. Therefore, our theory allows standard formulation in terms of nonlinear conductivity.

The shift of the chemical potential always occurs in the spin-valve device with injection, although in devices with direct ferromagnet–normal layer contact (without contact resistance) it has a slightly different form [18, 19]. Therefore, the nonlinear effects in magnetoresistance should be considered in all devices where the shift of the chemical potential of the order of applied voltage can significantly effect conductivity.

Let us consider the case when the transport in the organic layer is governed by the HOMO and LUMO. The voltage \( \sim 0.1 \) V is not sufficient to inject carriers into these states, and all the carriers in the HOMO and LUMO are thermally activated. The number of such carriers is small, and it allows us to neglect the space charge, making our theory applicable to this case. Transport via the HOMO and LUMO corresponds to the large energy \( \mathcal{E}_0 \sim 1 \) eV and leads to the exponential suppression of the spin-valve effect with applied voltage when \( eU > k_B T \) (see also [28]). This exponential suppression was never observed in the experiments. It gives another argument (besides those discussed in [16]) against the HOMO or LUMO transport in the organic spin-valves.

These arguments are in line with the arguments presented in [16] invoking the presence of impurity states in the organic gap to describe the organic SV devices. The nature of these states, however, is far from being clear. It was reported [17] that similar defects may be created during sample preparation, leading to the suppression of the spin-valve effect in sufficiently thick samples. The concentration of such defects can be very low (sub-percent level), precluding their detection by spectroscopic techniques [17]. The author of [16] considered impurity states with a concentration of \( \sim 10^{19} \) cm\(^{-3} \) and a broad distribution of energies. Such a broad distribution yields \( \sigma(\mu) \approx \text{const} \) and the discussed nonlinearity is absent. It was also assumed [16] that the organic layer is highly conductive and its resistance is negligible relative to contact resistances. Note that the conductivity of a system of localized states with a broad energy distribution is governed by a small number of states with energy close to the Fermi level [36]. Therefore, the actual concentration of impurities that contribute to conductivity is \( \sim 10^{17} \) cm\(^{-3} \), which can hardly lead to the high conductivity of the organic layer.

There are two possible solutions to this problem. The impurity states may be arranged in some sort of conducting channels or their energy distribution may be more narrow than assumed in [16]. The second option leads to the strong nonlinear phenomena related to \( \sigma(\mu) \) dependance. In this paper, we discussed these phenomena in the extreme case when the width of the energy distribution of impurity states is less than the temperature.

6. Conclusion

We derived a set of kinetic equations describing nonlinear effects related to the injection and transport of spin-polarized carriers in organic semiconductors with hopping conductivity. The model predicts a strongly voltage-dependent magnetoresistance split into three distinct regimes. The first regime (low voltages) corresponds to the well-known in inorganic spintronics conductivity mismatch limitation, underlining the correctness of the applied approach. The second regime at intermediate voltages corresponds to fully suppressed
magnetoresistance. Interestingly, a third regime develops at higher voltages and accounts for a novel and purely organic paradigm. It is promoted by strongly nonlinear effects in an organic semiconductor, whose strength is characterized by the dimensionless parameter $eU/k_BT$. This nonlinearity, depending on device condition, can lead to both significant enhancement or to exponential suppression of the spin-valve effect in organic devices. Consequently, while in inorganic devices, the conductivity mismatch limitation can be lifted off only by inserting a spin-dependent tunnelling resistance, organic devices feature an additional mechanism based on nonlinear charge transport behaviour.

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