Tunnel magnetoresistance of an organic molecule junction

Tunnel magnetoresistance of an organic molecule junction

Ashhadi Mojtaba [*]**, Shahtahmasebi Nasser, Vahedi Davoud, Askari Mostafa**
Department of Physics, Ferdowsi University of Mashhad, Mashhad, Iran
Nano Research Center of Ferdowsi University of Mashhad, Mashhad, Iran

E-mail: mojtaba_ash5@yahoo.com

Abstract. Coherent spin-dependent electronic transport is investigated in a molecular junction based on oligophenylene attached to two the semi-infinite ferromagnetic (FM) electrodes with finite cross sections. The work is based on the tight-binding Hamiltonian model and within the framework of a non-equilibrium Green's function (NEGF) technique. It is shown that tunnel magnetoresistance (TMR) of molecular junction can be large (over 60 %) by adjusting the related parameters, and depends on: (i) the applied voltages and (ii) the length of oligophenylele molecule.

1. Introduction

Spintronics is an exciting field of research where electron spin, in addition to charge, is exploited for electronic device application. The ability to manipulate and detect spin offers the potential of a new paradigm for electrical devices. It has been suggested that adding the spin degree of freedom to conventional charge-based electronic devices or using spin alone has the potential advantages of non-volatility, increased data processing speed, decreased electric power consumption, and increased integration densities compared with conventional semiconductor devices [1]. One of the most successful spintronic devices to date is the magnetic sensor composed of a magnetic tunnel junction exhibiting the tunneling magnetoresistance effect. Tunnel magnetoresistance effect in systems with spin-polarized transport is at the heart of spintronic [2] and has found important applications in information storage technology. A basic TMR device consists of a tunnel barrier separating two ferromagnetic (FM) metal layers which play the role of device leads. Magnetoresistance refers to a change in the electrical current when the relative magnetization of the ferromagnetic electrodes changes their alignment [3]. The TMR effect [4] originates from the quasi-particle electronic structure of the ferromagnetic electrodes which depends on their magnetization orientation. The tunneling conductance tends to be smallest when the orientations are opposite, leading to a spin valve character [4–8]. Recent experimental data have clearly demonstrated that spin-polarized injection and transport in molecular spintronic devices are not only possible, but also efficient. There have been several investigations of spin-transport through organic molecules. These include carbon nanotube spin valves [9], hot electron coherent spin transfer across molecular bridges [10], spin-injection in π-conjugated molecules [11-12] and organic tunneling junctions [13]. At the same time a few seminal theoretical studies on transport through 1, 4-benzene-dithiolate molecular spin-valves [14-15] and molecular magnets [16] have appeared. These calculations, based on density functional theory or tight-binding model, have shown that by changing the magnetic alignment of the contacts one can substantially affect the electronic current in the molecular devices. Recently charge transport of metal-molecule-metal junctions based on oligophenylenes has been investigated theoretically [17]. However, we believe that no theoretical study on spin-polarized transport through a molecular junction based on

oligophenylene and its TMR effect, based on tight-binding method, has so far been reported. In this paper, we calculate the spin currents through the oligophenylene molecule, sandwiched between two the semi-infinite FM electrodes with simple cubic structure and square cross section (*xy* plane). The model of such a structure is shown schematically in figure 1. This paper is organized as follows: in Section 2, we give a model and the description of the method. The results and discussion are presented in section 3, followed by a conclusion in section 4.
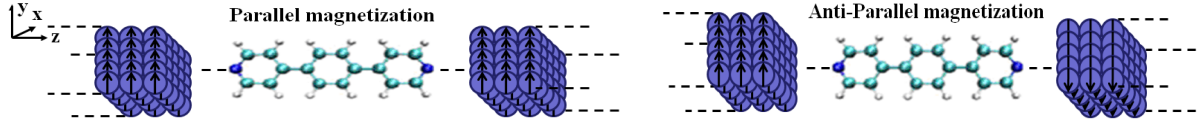
Figure 1. A schematic representation of the FM/oligophenylene/FM molecular junction in two configurations Parallel (P) and Anti-Parallel (AP) magnetization.

2. Methodology

Assuming elastic scattering and neglecting spin-flip scattering and spin precession in the tunneling process because of the weak spin-orbit and hyperfine interaction expected in the π-conjugated organic layer [11], this implies that spin up electrons only tunnel to and from spin up states, and vice versa. Spin currents between two the magnetic electrodes can be written as $I=I_\uparrow+I_\downarrow$, where $I_\uparrow$ and $I_\downarrow$ are the contributions from spin-up and spin-down states. In the low-bias limit, the spin currents as a function of the applied voltage V can be calculated in the framework of the Landauer-Büttiker formula based on the NEGF method [18]

$$I_\sigma(V) = \frac{e}{h} \int_{-\infty}^{+\infty} T_\sigma(\varepsilon,V)\big[f(\varepsilon-\mu_L) - f(\varepsilon-\mu_R)\big]d\varepsilon \qquad (1)$$

Here $\sigma=\uparrow,\downarrow$ is the spin index, f is the equilibrium Fermi distribution and $\mu_{L,R}=E_F\pm eV/2$ are the electro-chemical potentials of the electrodes in terms of the common Fermi energy E_F for the left (*L*) and right (*R*) electrodes. The transmission probability $T_\sigma(\varepsilon, V)$ can be expressed in terms of the Green's function of the molecule and the coupling of the system molecule with the two electrodes by the expression

$$T_\sigma(\varepsilon,V) = Tr[\Gamma_{L,\sigma} G_\sigma^r \Gamma_{R,\sigma} G_\sigma^a] \qquad (2)$$

where G_σ^r and G_σ^a are, respectively, the retarded and advanced Green's function of the molecule. The $\Gamma_{L(R),\sigma}$ is the coupling terms due to the coupling of the molecule with the (*L*) and (*R*) electrodes, respectively. For a complete system, i.e., the molecule with the two electrodes, the Green's function is defined as

$$G(\varepsilon) = ((\varepsilon+i\zeta) - H)^{-1} \qquad (3)$$

where ζ is a very small number which can be put as zero in the limiting approximation. The above Green's function corresponds to the inversion of an infinite matrix which consists of the finite molecule and the two semi-infinite electrodes. It can be partitioned into different sub-matrices that correspond to the individual sub-systems. The effective Green's function for the molecule can be written as

$$G_\sigma(\varepsilon,V) = \lim_{\zeta\to\infty}[(\varepsilon+i\zeta)I - H_M - \sum_{L,\sigma}(\varepsilon-eV/2) - \sum_{R,\sigma}(\varepsilon+eV/2)]^{-1} \qquad (4)$$

where H_M is the Hamiltonian for the oligophenylene molecule sandwiched between the two FM electrodes. Within the non-interacting picture, the tight-binding Hamiltonian of the molecular system can be manifested as [17]

$$H_M = \sum_{i,\sigma \in M} \varepsilon_{i,\sigma} c^+_{i,\sigma} c_{i,\sigma} + \sum_{i,\sigma \in M} (t_{i,i+1} c^+_{i,\sigma} c_{i+1,\sigma} + h.c.) \tag{5}$$

where $c^\dagger_{i,\sigma}(c_{i,\sigma})$ creates (destroys) an electron with spin σ at site i of the molecular system and $\varepsilon_{i,\sigma}$ is the on-site energy and $t_{i,i+1}$ is hopping integral and is equal to t' for the nearest neighbors. In the equation (4), $\Sigma_{L,\sigma} = h^\dagger_{LM} g_{L,\sigma} h_{LM}$ and $\Sigma_{R,\sigma} = h_{RM} g_{R,\sigma} h^\dagger_{RM}$ are the self-energy terms due to the two electrodes, $g_{L,\sigma}$ and $g_{R,\sigma}$ are, respectively, the surface Green's function for the (L) and (R) electrodes, $h_{\alpha M}$ is the coupling matrice and it will be non-zero only for the adjacent points in the molecule and the electrode $\alpha (=L,R)$. The coupling terms $\Gamma_{L,\sigma}$ and $\Gamma_{R,\sigma}$ for the molecule can be calculated through the expression[18]

$$\Gamma_{\alpha,\sigma} = i[\Sigma^r_{\alpha,\sigma} - \Sigma^a_{\alpha,\sigma}] \tag{6}$$

where the advanced self-energy $\Sigma^a_{\alpha,\sigma}$ is the Hermitian conjugate of the retarded self-energy $\Sigma^r_{\alpha,\sigma}$. Thus the coupling terms can be written as

$$\Gamma_{\alpha,\sigma} = -2\,\mathrm{Im}(\Sigma^r_{\alpha,\sigma}) \tag{7}$$

$g_{\alpha,\sigma}$ are the surface Green's functions of the uncoupled electrodes and their matrix elements are given by[19]

$$g_{\alpha,\sigma}(m,n;z) = \sum_{\mathbf{k}} \frac{\psi_{\mathbf{k}}(\mathbf{r}_m)\psi^*_{\mathbf{k}}(\mathbf{r}_n)}{z - \varepsilon_0 + \sigma.\mathbf{h}_\alpha + E(\mathbf{k})} \tag{8}$$

$\sigma.\mathbf{h}_\alpha$ is the internal exchange energy with $\mathbf{h}_\alpha$ denoting the molecule field on the electrodes and σ being the conventional Pauli spin operator. m,n shown site $m^{th}(n^{th})$ in electrode α, and $r_m \equiv (x_m, y_m, z_m)$, $\mathbf{k} \equiv (l_x, l_y, k_z)$, $z = \varepsilon + i\zeta$,

$$\psi_{\mathbf{k}}(\mathbf{r}_m) = \frac{2\sqrt{2}}{\sqrt{(N_x+1)(N_y+1)(N_z)}} \sin\left(\frac{l_x x_m \pi}{N_x+1}\right) \sin\left(\frac{l_y y_m \pi}{N_y+1}\right) \sin(k_z z_m) \tag{9}$$

and

$$E(\mathbf{k}) = 2t\left(\cos\left(\frac{l_x \pi}{N_x+1}\right) + \cos\left(\frac{l_y \pi}{N_y+1}\right) + \cos(k_z a)\right) \tag{10}$$

Here, $l_{x,y}(=1,...,N_{x,y})$ are integers, $k_z \in [-\pi/a, \pi/a]$, and N_β with $\beta = x,y,z$ is the number of lattice sites in the β direction. Note that N_x and N_y corresponds to the number of atoms at the cross-section of electrodes. ε_0 is the spin independent on-site energy in the electrodes, and will be set to $3t$ where t is the hopping strength between nearest-neighbor sites in the (L) and (R) electrodes and ε is injection energy of the transmitting electron.

By calculating the self-energies, the coupling terms $\Gamma_{L,\sigma}$ and $\Gamma_{R,\sigma}$ can be easily obtained and then the transmission probability (T_σ) and current (I_σ) will be computed from the expression as mentioned in equation (1) and (2). In the semi-infinite FM electrodes described by the single-band tight-binding model, only the central site at the cross section is connected to the molecule. In this case, tunnel magnetoresistance is defined as a relative change in the current of the system when the magnetizations of the two ferromagnetic layers switch between parallel (P) and anti-parallel (AP) configurations (figure 1), hence: $TMR \equiv (I_P \ I_{AP})/I_P$, where $I_{P,AP}$ are the total currents in the P and AP alignments of magnetizations in the FM electrodes, respectively.

3. Results and discussion

Based on the formalism described in section 2, we have investigated the coherent spin-depended transport and magnetoresistance effect of FM/oligophenylene/FM molecular junction. In our considered system, the magnetization orientation (i.e. the spins direction) in the left electrode stays fixed (in the $+y$ direction) but the other right electrode is free and may be switched back and forth by an external magnetic field (in the $+y$ or $-y$ directions) (see figure 1). Thus, when the magnetizations of two FM electrodes are parallel, spin-up and spin-down electrons see a symmetric structure, while for the anti-parallel alignment these electrons see an asymmetric structure.

We set $\varepsilon_{i,\sigma} = 0$, $|h_\alpha| = 1.5\ eV$, $N_x = N_y = 5$, $t = 1eV$, $T = 300K$, $t' = 1.2eV$ [17], and consider molecule-to-electrode coupling strength equal to $0.5eV$ in the calculations.

In figure 2, we present the transmission logarithm at zero applied voltage for the P and AP alignments for the oligophenylene molecule. Study of this figures (Panels (a) and (b)) shows that each the energy peak in transmission logarithm due to matching of the energy of the incident electron with energy eigenvalue of the molecule. The curves shown an oscillatory behavior when the electrons transport through molecule it means that the molecular levels are quantized. The electrons with spin-up or spin-down can transport through the molecule only when a resonance occurs between the molecular level and the incident electronic energy. As a result, resonance peaks are produced, therefore, we can predict that this resonance peaks are a fingerprint of the electronic structure of the molecule.

The calculated current-voltage (I–V) curves for the oligophenylene molecule attached to FM electrodes are shown in figure 3 for P and AP alignment. As can be seen, the current for the P alignment reaches bigger values in comparison with the current for the AP, because of the difference between surface density of states of the FM electrodes for spin-up and spin-down electrons. This difference in the surface density of states of the FM electrodes causes the electrons with P magnetic alignment than electrons with AP magnetic alignment to have a more likely in probability transmission (figure 2).
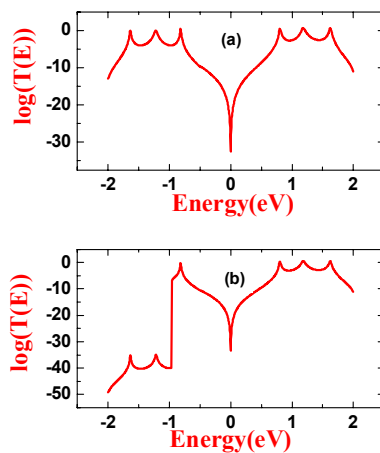

Figure 2. Panels (a) and (b) show the logarithm of the transmission coefficient at zero applied voltage versus energy for P (a) AP (b) magnetic alignment and for $N=3$,(N is the length of the oligophenylene molecule).
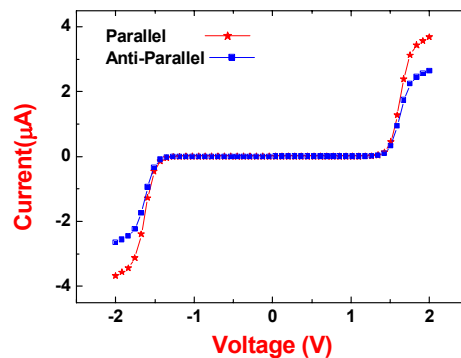
Figure 3. Spin currents for P (stars) and AP (squares) versus applied voltage and $N=3$.

The effect of an applied voltage is that of shifting the chemical potentials of the two electrodes relative to each other by *eV*, with *e* the electronic charge. Currents will flow whenever a molecular level (either the highest occupied molecular orbital or the lowest unoccupied molecular orbital) is positioned within such a bias window. The appearing of molecular levels in the bias window when the potential is increased typically leads to changes in the slope and a step-like behavior of the *I-V* characteristics.

The FM electrodes have unbalanced spin-up and spin-down electrons near its Fermi level, the tunneling channels for spin-up and spin-down electrons are explicitly separated. The electrons with magnetic moment P to the magnetization are electrons of majority-spin, and with magnetic moment AP to the magnetization are electrons of minority-spin. More specifically, in P spin configuration, the majority spin is spin-up and the minority spin is spin-down for both the electrodes, whereas in AP configuration, the majority spin is spin-up on one electrode and spin-down on the other. Consequently, the P arrangement gives much higher total current through the molecule than does the AP arrangement. This difference in the total currents is the origin of TMR effect which has been shown in figure 4.
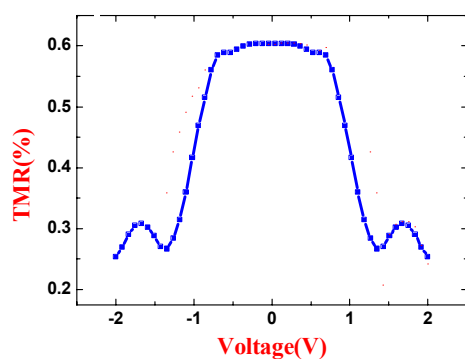
Figure 4. TMR as a function of applied voltage and for *N=3*.
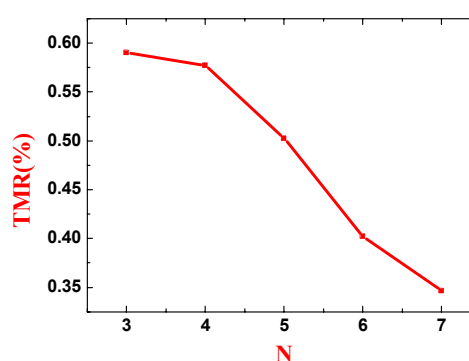
Figure 5. TMR as a function of varying lengths (*N=3… 7*) with *V=0.5eV* attached to the ferromagnetic electrodes.

The TMR ratio has it maximum value (more than 60%) at low bias voltages. With increasing the applied voltage, we first observe that the TMR decreases and with further increase in the bias voltage, the TMR ratio increases and then, the reduction and enhancement of TMR are repeated. The reason is that with increasing bias voltage the current of tunneling through the junction increases significantly, however, the difference of current for the parallel magnetization alignment from that for alternately anti-parallel magnetization alignment increases only slightly. This leads to the decrease of TMR monotonously with increasing bias voltage. Our results are qualitatively in agreement with the experimental measurements [20, 21]. Finally, in figure 5 we show the changes of the TMR due to the increase the length of oligophenylene molecule in the junction with *V=0.5eV*. Here we can see that the TMR decrease when length of the molecule increase. The origin of the trend of decreasing TMR reflects the increasing of states in the junction and thus the current is increased. Note the Similar behavior in refs. [22-24] has been shown that TMR is decreased with increasing thickness of molecule.

4. Conclusion

Using the NEGF method and within the framework of the tight-binding Hamiltonian model, we have investigated the possibility of making an oligophenylene molecule-based magnetic tunnel junction.

We have shown that the coupling between the molecular system and magnetic electrodes in FM/oligophenylene/FM structure produces large magnetoresistance effects (greater than 60%) that can be strongly depends on: (i) the applied voltages and (ii) the length of molecule.

Throughout this study, we have ignored the effects of inelastic scattering such as: the electron-phonon interaction, electron–electron correlation, etc. These factors can affect the spin-dependent transport. Another improved method is needed for better results and we need further study for considering all these effects

References
[1] Wolf S A, Chtchelkanova A Y and Treger D M 2006 *IBM J. RES & DEV.* **50** 101
[2] Wolf S A, Awschalom D D, Buhrman R A, Daughton J M, von Molnar S, Roukes M L, Chtchelkanova A Y and Treger D M 2001 *Science* **294** 1488
[3] Zutic I, Fabian J and Das Sarma S 2004 *Rev. Mod. Phys.* **76**, 323
[4] Slonczewski J C 1989 *Phys. Rev. B* **39** 6995
[5] Julliere M 1975 *Phys. Lett. A* **54** 225
[6] Bratkovsky A M 1997 *Phys. Rev. B* **56** 2344
[7] Wang B G, Wang J and Guo H 2001 *J. Phys. Soc. Jpn.* **70** 2645
[8] Mireles F and Kirczenow G 2002 *Phys. Rev. B* **66** 214415
[9] Tsukagoshi K, Alphenaar B H and Ago H 1999 *Nature* **401** 572
[10] Ouyang M and Awschalom D D 2003 *Science* **301** 1074
[11] Xiong Z H, Wu D, Valy Vardeny Z and Shi J 2004 *Nature* **427** 821
[12] Dediu V, Murgia M, Matacotta F C, Taliani C and Barbanera S 2002 *Solid State Commun.* **122** 181
[13] Petta J R, Slater S K and Ralph D C 2004 *Phys. Rev. Lett.* **93** 136601
[14] Pati R, Sanapati L, Ajayan P M and Nayak K 2003 *Phys. Rev. B* **68** 100407
[15] Emberly E G and Kirczenow G 2002 *Chem. Phys.* **281** 311
[16] Kim G H and Kim T S 2004 *Phys. Rev. Lett.* **92** 137203
[17] Viljas J K, Pauly F and Cuevas J C 2008 *Phys. Rev. B* **77** 155119
[18] Datta S 1997 *Electronic Transport in Mesocopic System* (Cambridge University Press, Cambridge)
[19] Yoshihiro A and Hidetoshi F 2005 *Phys. Rev. B* **72** 085431
[20] Moodera J S, Kinder L R, Wong T M and et al. 1995 *Phys. Rev. Lett.* **74** 3273
[21] Moodera J S, Kinder L R 1996 *J. Appl. Phys.* **79** 4724
[22] Sun J J, Sousa R C, Galvao T T P, Soares V and Freitas P P 1999 *J. Magn. Soc. Japan* **23** 55
[23] Szulczewski G, Tokuc H, Oguz K and Coey J M D 2009 *Appl. Phys. Lett.* **95** 202506
[24] Davis A H and MacLaren J M 2002 *J. Phys.: Condens. Matter* **14** 4365