Spin-dependent rectification in the $C_{59}N$ molecule

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Abstract. Coherent spin-dependent electron transport is investigated in three conditions: (1) a C_{60} molecule is connected to two ferromagnetic (FM) electrodes symmetrically, (2) a $C_{59}N$ molecule is connected to two FM electrodes symmetrically and (3) a $C_{59}N$ molecule is connected to two FM electrodes asymmetrically. This work is based on a single-band tight-binding model Hamiltonian and the Green's function approach with the Landauer–Buttiker formalism. Electrodes used in this study are semi-infinite FM electrodes with finite cross-section. Obvious rectification effect is observed in the $C_{59}N$ molecule which is connected to the FM electrodes asymmetrically. This effect is more in the P alignment of FM electrodes than in AP alignment of FM electrodes. This study indicates that the rectification behaviour is due to the asymmetry in molecule and junctions. Also in this investigation tunnel magnetoresistance (TMR) is calculated for these molecules. Asymmetry is observed in TMR of $C_{59}N$ which is coupled to the electrodes asymmetrically due to asymmetric junctions, but TMR of C_{60} is symmetric.

Keywords. Spin-dependent electron transport; C_{60} molecule; $C_{59}N$ molecule; rectification effect; tunnel magnetoresistance.

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1. Introduction

The azafullerene, $C_{59}N$, represents an exciting addition to the family of fullerene derivatives. In this molecule, a single carbon atom of the C_{60} fullerene cage is replaced by a group V nitrogen atom. Electron rectification occurs when $I(V) \neq I(-V)$. This is due to the asymmetry in the structure or junctions [1–7]. These asymmetries are responsible for different behaviours of the molecule in the electron transport through electrodes in the positive and negative voltages and thus electron rectification takes place. Lakshmi and Pati [8] considered a molecule which was connected to electrodes, had donor and acceptor parts with positive and negative on-site energies. They believed that different on-site energies in these parts led to localize electrons in near-zero energies with negative on-site energies. Consequently, rectification was seen in $I-V$ characteristics. Miller *et al* showed that the reason behind rectification could be the unequal number of

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open-shell excitation channels at opposite bias voltages [9]. Several investigations were done in the field of spin-dependent electron transport through FM electrodes [10–22]. In recent years, spin-dependent electron rectification was studied in a few theoretical studies [23,24]. Kuo *et al* showed that in a nonlinear response regime, the electron spin singlet and triplet states could be determined by current rectification behaviour which arose from space symmetry breaking [25]. Many of 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 in many types of molecules. The fullerene C_{60}, which is one of the most well-known organic semiconductors, is placed as a bridge in magnetic tunnel junctions, because its lowest unoccupied molecular orbital (LUMO) is located at relatively lower energies. The spin-dependent transport in FM/C_{60}/FM junction was studied [26], but spin-dependent transport through a single $C_{59}N$ molecule, based on tight-binding method, has not been reported.

Tunnel magnetoresistance (TMR) is defined as a magnetoresistive effect that occurs in a magnetic tunnel junction (MTJ). While many studies have dealt with calculation of TMR for nanostructures [27–36], in some others, asymmetric TMR as a function of voltage were studied [34–36].

In this paper, the role of asymmetries on the spin-dependent electron rectification and TMR ratio are investigated.

2. Methodology

Electron spin-dependent currents between two magnetic FM electrodes can be defined as $I = I_{\uparrow} + I_{\downarrow}$, where $I_{\uparrow}$ and $I_{\downarrow}$ are defined as the up-spin and down-spin current flows from one FM electrode to another, respectively. The rectification current is $I_r(V) = [I(V) + I(-V)]/2$. Spin current rectification is defined as a different definition in ref. [37]. Current can be determined using Landauer–Buttiker formula, which is based on negative equilibrium Green's function (NEGF) method [38]:

$$I_{\sigma} = \frac{e}{h} \int_{-\infty}^{+\infty} T_{\sigma}(E, V_a) \left[f(E - \mu_L) - f(E - \mu_R) \right] \mathrm{d}E. \tag{1}$$

Here, $\sigma = \uparrow, \downarrow$ is the spin index, f is the equilibrium Fermi function and $\mu_{L,R}$ stands for the electronic chemical potential of the left (right) leads whose values depend on the applied bias voltage. In this investigation, we consider asymmetric junctions to obtain rectification behaviour in the $I-V$ curve for $C_{59}N$. So, we choose different coupling strength to connect molecules to the FM electrodes. Based on the investigation done by Zhang *et al* [39], we set more bias voltage drop on the weakly coupled right junction and less potential drop on the strongly coupled left junction. The electronic chemical potential of the two electrodes can be given as follows:

$$\mu_L = E_f + \eta eV \tag{2}$$

and

$$\mu_R = E_f - (1 - \eta)eV, \tag{3}$$

where e is the electron charge, $\eta < 0.5$ for the asymmetric junction and $\eta = 0.5$ for the symmetric junction. We choose $\eta = 0.25$ for the asymmetric junction in this study. V is the source–drain applied voltage, E_f is the equilibrium Fermi energy chosen here as 0 eV. The transmission probability $T_\sigma(E, V_a)$ can be expressed as follows:

$$T_\sigma(E, V_a) = \mathrm{Tr}\left[\Gamma_{L,\sigma} G_\sigma^r \Gamma_{R,\sigma} G_\sigma^a\right], \tag{4}$$

where G_σ^r and G_σ^a are known as the retarded and advanced Green's function of the molecule, respectively. $\Gamma_{L(R),\sigma}$ denotes the coupling terms, which are obtained due to the coupling of the molecule with the (L) and (R) electrodes, respectively. For this system which consists of a molecule with two electrodes, Green's function is given by

$$G(E) = ((E + i\xi) - H)^{-1}, \tag{5}$$

where E is the injected electron energy and ξ is a very small number taken as zero in the limiting approximation. The above Green's function is calculated by the inversion of an infinite matrix which contains finite molecule and two semi-infinite FM electrodes. It can be divided into different submatrices according to the individual subsystems. Effective Green's function for the molecule is given by

$$G_\sigma(E, V_a) = \lim_{\zeta \to 0}\left[(E + i\xi)I - H_M - \sum_{L,\sigma}(E - \mu_L) - \sum_{R,\sigma}(E - \mu_R)\right]^{-1}. \tag{6}$$

H_M is the Hamiltonian related to the molecule which is used in this investigation. Parida *et al* [40] considered a four-site system to study transport through a molecule, where current flowed through two central sites and lateral sites behaved as the source electrodes. They proposed an asymmetric junction, by considering negative and positive on-site energies at second and third sites. This asymmetry resulted in rectification current. However, we consider a 60-site system and an asymmetric junction is studied by inserting different coupling strengths between a molecule and FM electrodes. For the first state, H_M is the Hamiltonian of the C$_{60}$ molecule, as follows [41]:

$$H_M = \sum_{i_M,\sigma} \varepsilon_{i_M} c_{i_M,\sigma}^+ c_{i_M,\sigma} - \sum_{\langle i_M, j_M\rangle,\sigma} t_{i_M, j_M} \hat{c}_{i_M,\sigma}^+ \hat{c}_{j_M,\sigma}, \tag{7}$$

where $c_{i_M,\sigma}^+ (c_{i_M,\sigma})$ creates (destroys) an electron with spin σ at site i of C$_{60}$ and ε_{i_M} is the on-site energy and will be set to zero. The hoping strength t_{i_M, j_M} in C$_{60}$ molecule depends on the C–C bond length; thus, we assume different hoping matrix elements: t_1 for the single bonds and t_2 for the double bonds. The Hamiltonian of C$_{59}$N is defined as

$$H_M = H_{C_{60}} + H_S, \tag{8}$$

where H_S and $H_{C_{60}}$ are the Hamiltonians to inject nitrogen atom to the C$_{60}$ molecule and Hamiltonian for the C$_{60}$ molecule which is defined above, respectively. H_S is defined as

$$H_S = \sum_\sigma \varepsilon_{k_S} b_{k_S,\sigma}^+ b_{k_S,\sigma} - \sum_{l_S,\sigma} t'_{k_S,l_S} b_{k_S,\sigma}^+ b_{l_S,\sigma}, \tag{9}$$

where ε_{k_S} is the on-site energy for the nitrogen atom with spin σ replaced in the kth site. $b_{k_S,\sigma}^+ (b_{k_S,\sigma})$ creates (destroys) an electron with spin σ in the kth site. t'_{k_S,l_S} is the element

of hopping matrix between the kth site and the nearest neighbour, which is in the lth site. In eq. (4), $\Sigma_{L,\sigma} = h_{LM}^+ g_{L,\sigma} h_{LM}$ and $\Sigma_{R,\sigma} = h_{RM} g_{R,\sigma} h_{RM}^+$ represent the self- energy terms due to the two electrodes, $g_{L,\sigma}$ and $g_{R,\sigma}$ reflect the surface Green's function for the (L) and (R) electrodes, respectively; $h_{\alpha M}$ is the coupling matrix 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 estimated through the expression [38]

$$\Gamma_{\alpha,\sigma} = i \left[\Sigma_{\alpha,\sigma}^r - \Sigma_{\alpha,\sigma}^a \right], \tag{10}$$

where the advanced self-energy $\Sigma_{\alpha,\sigma}^a$ denotes the Hermitian conjugate of the retarded self-energy $\Sigma_{\alpha,\sigma}^r$. Thus, the coupling terms are given by

$$\Gamma_{\alpha,\sigma} = -2 \operatorname{Im}\left(\Sigma_{\alpha,\sigma}^r\right). \tag{11}$$

$g_{\alpha,\sigma}$ reflects the surface Green's functions of the uncoupled FM electrodes and their matrix elements are [42]:

$$g_\sigma(m, n, z) = \sum_k \frac{\psi_k(r_m)\psi_k^+(r_n)}{z - \varepsilon_0 + \sigma h_\alpha + E(k)}. \tag{12}$$

σh_α represents the internal exchange energy where h_α denotes the molecular field on the FM electrodes and σ the conventional Pauli spin operator, m, n show site mth (nth) in FM electrode α, and $r_m \equiv (x_m, y_m, z_m)$, $k \equiv (l_x, l_y, k_z)$, $z = E + i\xi$,

$$\psi_k(r_m) = \frac{2\sqrt{2}}{\sqrt{(N_x+1)(N_y+1)\,(N_z)}} \sin\left(\frac{l_x x_m \pi}{N_x+1}\right) \sin\left(\frac{l_y y_m \pi}{N_y+1}\right) \sin(k_z z_m) \tag{13}$$

and

$$E(k) = 2t \left(\cos\left(\frac{l_x \pi}{N_x+1}\right) + \cos\left(\frac{l_y \pi}{N_y+1}\right) + \cos(k_z a) \right). \tag{14}$$

Here, $l_{x,y}(= 1, ..., N_{x,y})$ are taken as integers, $k_z \in [-\pi/a, \pi/a]$ and N_β with $\beta = x, y, z$ show the number of lattice sites in the β direction. Note that N_x and N_y denote the number of atoms at the cross-section of FM electrodes. ε_0 is the spin-independent on-site energy in the FM electrodes, and is taken as $3t$ where t reflects the hopping strength between nearest-neighbour sites in the (L) and (R) FM electrodes and ε is the injection energy of the transmitting electron. The coupling terms $\Gamma_{L,\sigma}$ and $\Gamma_{R,\sigma}$ can be easily obtained by calculating the self-energies and then the transmission probability $(T_{P,(AP)}(E) = T_{\uparrow\uparrow(\uparrow\downarrow)}(E) + T_{\downarrow\downarrow(\downarrow\uparrow)}(E))$ and current $(I_{P,AP})$ will be determined from the expression as mentioned in eqs (1) and (2), where $T_{P,(AP)}$ and $I_{P,(AP)}$ are the total transmissions and currents in the P and AP alignments of magnetizations in the FM electrodes, respectively. TMR is interpreted as a relative change in the current of the system

when the parallel and antiparallel alignments of magnetizations switch (see figure 1). Hence

$$\text{TMR} = \left(I_\text{P} - I_\text{AP} \right) / I_\text{P}.$$

3. Results and discussion

We used these parameters: $\varepsilon_{i_M} = 0$ eV, $t_1 = 2.5$ eV, $t_2 = 1.1 * 2.5$ [41], $\varepsilon_{k_S} = 0$ eV, $t'_{k_S, l_S} = 1.05$ eV [43], $h_\alpha = 1.5$ eV, $T = 300$ K, $N_x = N_y = 5$, $t = 1$ eV. For symmetric junction, consider molecule-to-FM electrode coupling strength equal to 0.5 eV. Count for asymmetric junction molecule-to-left FM electrode is 0.75 eV and molecule-to-right FM electrode is 0.25 eV. Figures 1a and 1b are related to alignments of FM electrodes with parallel (P) magnetic moment arrangements and antiparallel (AP) magnetic moment arrangements, respectively and C_{60} molecule is between two FM electrodes. Figure 2 shows logarithm of transmission for C_{60} and $C_{59}N$, which are connected to the FM electrodes symmetrically. In $C_{59}N$ molecule, more resonant peaks appear in the logarithm of transmission spectrum, which reveals that more energy levels appear in the system. In this figure, we present transmission probability in the P alignment which is bigger than AP alignment and these differences are due to the σh_α interaction term. For example, in the P alignment, when one spin-up electron is transported through the molecule from one FM electrode to the other one, where both these FM electrodes have spin-up magnetic moments, the spin of the electron interacts with the field which is parallel to the field created by the magnetic moment of this electron. In the AP alignment, when electron of the above example enters another FM electrode which has spin-down magnetic moments, spin of this electron interacts with the field which is antiparallel to the field created by


(a)

(b)
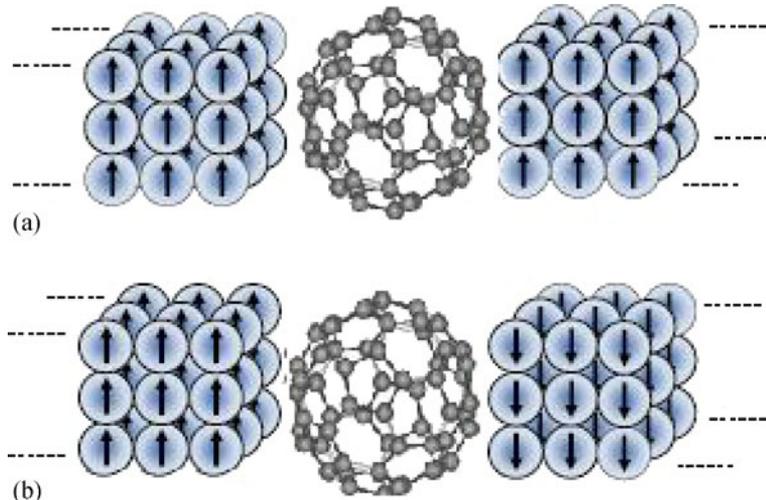
Figure 1. (**a**) FM–C_{60}–FM system in P alignment, (**b**) FM–C_{60}–FM system in AP alignment.
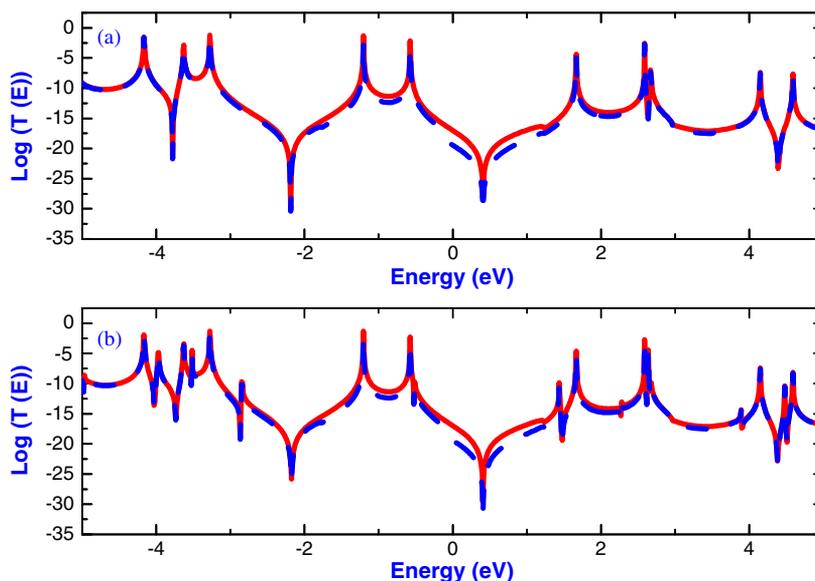
Figure 2. Logarithm of transmission at zero applied voltage vs. energy for P (red bold line) and AP (blue dash line) alignments for (**a**) C_{60} with symmetric junctions and (**b**) $C_{59}N$ with symmetric junctions.

the magnetic moment of this electron. So, electrons in the P alignment are more easily transported than electron in the AP alignment, from one FM electrode to another FM electrode. Consequently, transmission probability in the P alignment is more than in AP alignment.

Figures 3a and 3b show spin-dependent currents for C_{60} and $C_{59}N$ respectively, which have symmetric junctions that are plotted for P and AP alignments. In figures 3a and 3b, currents of P alignment are bigger than that of AP alignment because the transmission probability for P alignment is bigger than that for AP alignment. We can observe that current is nearly zero between -1 V and 1 V. As in ref. [44], these behaviours are due to spin blockade. Spin blockade arises from the weak coupling of molecules to FM electrodes. Figure 3a indicates that these currents are symmetric and figure 3c shows nearly symmetric curves. It is important to state that molecular rectifiers based on asymmetries of the leads-to-molecule coupling have been predicted, for example in a carbon conjugated-bond bridge [45] and in the 'tour wire' [46]. In this investigation, we observe that the asymmetric structure of $C_{59}N$ cannot lead to obvious rectification. So, to obtain spin-dependent electron rectification, we connect $C_{59}N$ to the FM electrodes asymmetrically. Figure 3b indicates spin-dependent electron currents for $C_{59}N$, which is connected to the FM electrodes asymmetrically for P and AP alignments. At forward bias, with increasing voltage, currents increase. $I–V$ curves for P and AP alignments have asymmetric behaviours against voltages. Currents flow at forward bias and they are nearly zero at reverse bias, and the junctions rectify. An important quantity that is calculated in the spin-dependent studies is the TMR ratio. As shown in figure 3d the largest values of
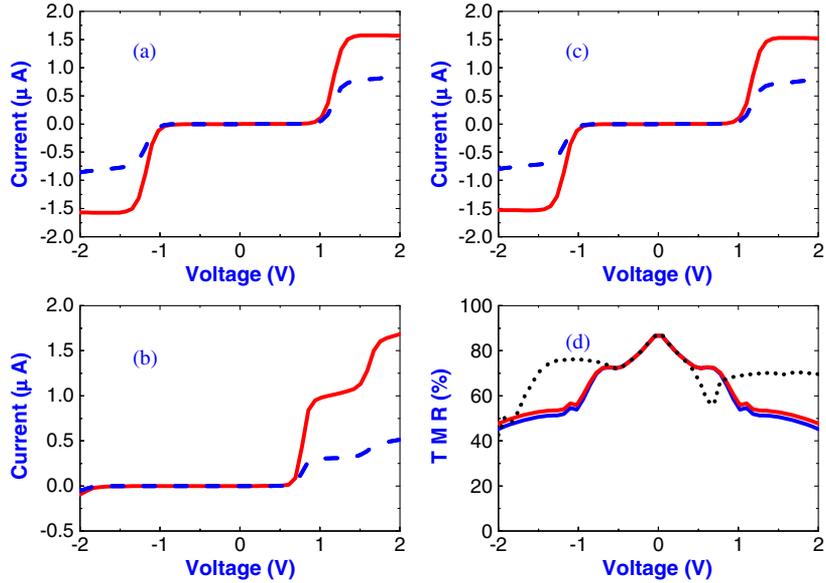
Figure 3. Currents for P (red bold line) and AP (blue dash line) vs. bias voltage for (**a**) C$_{60}$ with symmetric junctions, (**b**) C$_{59}$N with asymmetric junctions, (**c**) C$_{59}$N with symmetric junctions and (**d**) TMR as a function of applied voltage for C$_{60}$ with symmetric junctions (blue bold line) and C$_{59}$N with symmetric junctions (red bold line) and C$_{59}$N with asymmetric junctions (black dot line).
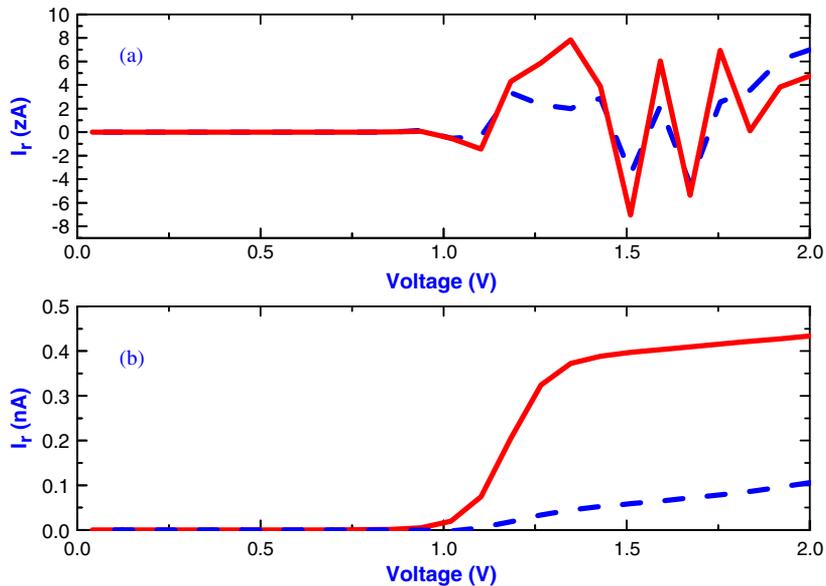
Figure 4. Rectification currents for P (red bold line) and AP (blue dash line) vs. bias voltage for (**a**) C$_{60}$ with symmetric junctions (in this panel $zA = 10^{-21}$A), (**b**) C$_{59}$N with symmetric junctions.
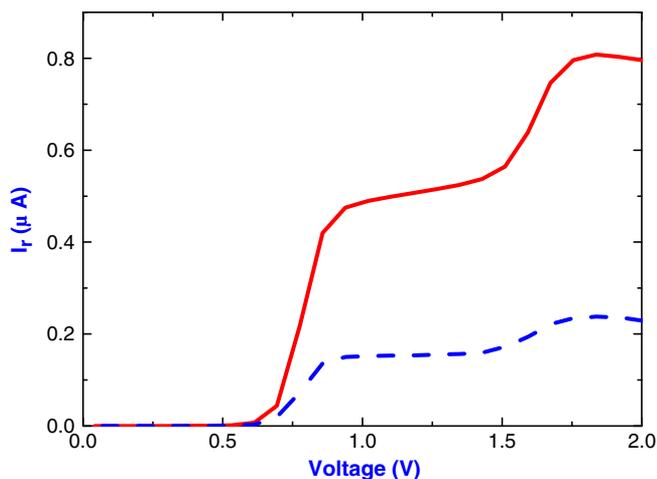
Figure 5. Rectification currents for P (red bold line) and AP (blue dash line) vs. bias voltage for $C_{59}N$ with asymmetric junctions.

TMR (85%) are observed in the low voltages. After these maximums, the TMR ratios decrease. In voltages which are further than 1 V and −1 V, TMR ratio of $C_{59}N$ is larger than TMR ratio of C_{60}. TMR curve of $C_{59}N$ which is connected to the FM electrodes asymmetrically, is asymmetric due to asymmetric P and AP currents. In this curve, at forward bias with increasing bias voltage, there is a sharp drop in TMR and then TMR increases with sharp slope. After this sharp slope, TMR very slowly increases. At reverse bias, reduction of TMR with increasing voltages is smaller than at forward bias. From this curve, we observe that after this reduction, TMR relatively increases and then starts to decrease. From figure 4a, we observe that spin-dependent electron rectification currents for C_{60} are $\left(I_r \approx 10^{-15} I\right)$ negligible and figure 4b, for $C_{59}N$ with symmetric junctions, shows small current rectification $\left(I_r \approx 10^{-4} I\right)$. As shown in figure 5, spin-dependent rectification currents for $C_{59}N$, with asymmetric junctions, have relatively large values. Also figures 4 and 5 indicate that rectification currents in the P alignment are bigger than that in AP alignment. From these observations, we can expect rectification behaviour to arise from asymmetries.

4. Conclusions

Using NEGF method and within the framework of tight-binding Hamiltonian model, we have investigated TMR and the possibility of spin-dependent rectification behaviour in C_{60} and $C_{59}N$. We have shown that spin-dependent rectifying behaviour in C_{60}, which has symmetric junctions, is negligible; and this effect is small for $C_{59}N$, which is connected to the FM electrodes symmetrically. However this behaviour obviously has been observed in $C_{59}N$, which is connected to the FM electrodes asymmetrically; and in this molecule by increasing the voltage, these rectification currents increase for P and AP alignments.

Also, asymmetric TMR ratio is observed in this system. These behaviours are due to the asymmetry in the coupling between the molecule and FM electrodes. The TMR ratio for C$_{60}$ is observed to be symmetric.

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