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Effects of dimerization and spin polarization on the conductance of a molecular wire

Sheelan Sengupta¹, S Lakshmi¹ and Swapan K Pati^{1,2}

¹ Theoretical Sciences Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur Campus, Bangalore 560 064, India

² DST Unit on Nanoscience, Jakkur Campus, Bangalore 560 064, India

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Abstract

We have studied the effects of dimerization on the energy levels of a one-dimensional molecular chain attached between two electrodes. Analytic expressions for the change in energies in the presence of a small perturbing external potential have been obtained for the three limiting cases: (a) uniform, (b) partially dimerized and (c) completely dimerized chains. We find that the presence of dimerization enhances the mixing between low-lying energies in the system resulting in a situation conducive to showing negative differential resistance (NDR) in the current–voltage characteristics. The effect of spin-polarized molecule–electrode couplings on a dimerized chain has also been studied, where both spin-parallel and spin-antiparallel current show NDR behaviour. Strong dimerization however is found to destroy the spin-valve effects that are most essential for spintronic devices.

1. Introduction

Recent success in the chemical synthesis of molecular wires and their potential use as devices in molecular electronics has spurred a renewed interest in the study of these mesoscopic devices [1–17]. Several experimental groups have reported transport measurements on a single molecule or small groups of molecules [4, 5, 8, 11, 17], demonstrating them to show conducting, rectifying and switching behaviour. A large amount of theoretical work based on semi-empirical to *ab initio* methods has also been performed to model molecular transport characteristics [5]. These theoretical studies have mainly focused on the mechanisms by which they conduct, how they operate under the influence of an external driving potential, and the recognition of the basic principles for achieving conductance control [6, 7, 9, 10, 12–14, 16].

It is quite well known by now that the current in these systems is a nonlinear function of the voltage and depends crucially on the electronic structure of the wire, the detailed structure of the contacts and the molecule–electrode couplings. The negative differential resistance (NDR) effect [18–20], which is characterized by the phenomenon of decreasing current with

increasing voltages, is a peculiar property of such devices and has been observed recently in some experiments on Tour molecules [6]. This property has wide application in many devices, including fast switches, oscillators and frequency locking circuits [21].

Together with the charge degrees of freedom, the manipulation of electronic spin in semiconductor devices led to the field of spintronics many years ago. The spin orientation of the electrons survives for a long period of time (of the order of \sim ns), and this makes it attractive for various applications. The concept that an electric current in a transition metal ferromagnet could be composed of spin-polarized carriers was introduced by Mott [22] and the idea was experimentally verified much later [23]. However, recently, the magnetic tunnel junction (MTJ) technique [24], using various transition metal ferromagnetic electrodes, has produced dominant spintronic devices [25] with a recent report of the high value of room-temperature magnetoresistance (MR) in these devices [26]. Devices consisting of pristine multiwall carbon nanotubes (CNTs) between metallic ferromagnetic electrodes have also been reported to exhibit MR effects up to 10% and more at 4.3 K [27] in the first approach towards a CNT-based spintronics. Electron transmission through insulating octanethiol molecular self-assembled monolayers (SAMs) between Ni contacts [28] and through 100 nm organic molecular films with magnetic electrodes have also been studied experimentally [29, 30].

However, theoretical studies of the dependence of current on different spin orientations have not received much attention until now. It has been recently predicted that molecules, connected between two ferromagnetic electrodes, can be utilized for building ultra-small spintronic devices that take advantage of weak molecular spin-orbit interaction to maximize the magnetoresistance effects [31–34]. Emberly *et al* have provided theoretical proof of the spin-valve behaviour observed in Ni break junctions bridged by an SAM of 1,4 benzene dithiolate molecules [31]. There are also a few other theoretical studies on spin-dependent charge transfer through single organic molecules connected between a pair of ferromagnetic electrodes [35, 36].

In most of these devices, the molecule is essentially a finite system with spatial broken symmetry. In particular, the translational invariance is broken, leading to dimerization in the system. Dimerized systems have been studied earlier by us using the Su–Schreiffer–Heeger (SSH) Hamiltonian, in which the dimerization sets in due to relaxation of the undimerized structure. In fact, both dimerized and charge asymmetric systems were shown to exhibit NDR features as found in certain Tour molecules [14, 18]. It was shown that an external bias can change the dimerized structure from one kind of insulating phase to the other through a phase which has uniform bond lengths (zero dimerization) and hence shows a high value of current. A similar situation occurred in the case of an initial charge-asymmetric structure, which, in the presence of an applied field, produced a neutral structure and exhibited NDR behaviour [18]. However a detailed analysis of the dimerization dependence of tunnelling current and NDR features in the presence of spin-polarized molecule–electrode coupling is clearly missing. In this paper, we discuss the extent of modifications of the low-energy levels with the application of a small perturbing bias of a molecular chain with different degrees of dimerization. We also study the current–voltage characteristics with different spin (parallel and antiparallel) polarizations in the electrodes to understand the role of dimerization on the spin-polarized current.

The paper is organized as follows. In the next section we present the model and the method of calculations. In sections 3.1 and 3.2, we discuss the effect of dimerization on the energy levels and on the tunnelling current of a one-dimensional molecular chain without and with spin polarizations. The spin polarization is considered when the molecule is connected between partially polarized ferromagnetic electrodes. We end the paper with a summary of all the results.

2. The model and the method

We consider a finite one-dimensional molecular wire coupled to two metallic electrodes at either ends. The electrode–wire coupling is assumed to occur only between the end sites of the wire and the corresponding electrodes. The direct or through-space coupling between the electrodes is neglected. The molecular wire consists of N sites. The electrodes are assumed to be non-interacting and composed of a continuum of states. They play the role of carrier reservoirs. The molecular wire is described by a tight-binding Hamiltonian of the form

$$H = \sum_{i,\sigma} \epsilon_{i,\sigma} (a_{i,\sigma}^\dagger a_{i,\sigma}) - \sum_{i,\sigma} (t + (-1)^{i+1} \delta t) (a_{i,\sigma}^\dagger a_{i+1,\sigma} + \text{hc}) \quad (1)$$

where t is the nearest-neighbour hopping integral, δt is the bond-alternation parameter, and ϵ_i the on-site potential at the i th site. We assume that $\epsilon_i = 0$ at all sites, as it corresponds to just diagonal energy shifts. We also set $t = 1$, and express the energies in units of t . The model is easily solvable, and the solution gives a set of energy levels in which the eigenstates corresponding to alternate levels have opposite spatial parity.

The non-equilibrium current is calculated using Landauer's formalism [37] at zero temperature as

$$I(V) = \frac{2e}{h} \int_{E_F - eV}^{E_F} \text{Tr}[\Gamma_L G \Gamma_R G] dE. \quad (2)$$

Here, V is the applied voltage, E is the electron injection energy and G is the voltage-dependent Green's function of the wire. $\Gamma_{L,R} = i(\Sigma_{L,R} - \Sigma_{L,R}^\dagger)$ describe the broadening of the energy levels due to the left and right electrodes' self-energies $\Sigma_{L,R}$.

In our calculation, we consider the electrostatic potential profile due to the applied bias to be a ramp function, decreasing linearly from one electrode to the other. We enforce that the left electrode has zero bias and the right electrode has full bias (V). This is to say that the electrodes are not polarized due to the accumulation of charges at the molecular sites. This happens when there are strong electron–electron correlations [38] in the molecule or, equivalently, when the electron charging energies are high. Hence, although we have not included charging energies explicitly in our model, this profile captures its effect, albeit qualitatively. However, to take into account any residual charge in the molecule in the presence of external bias, which can polarize the electrodes due to image potential, we perform a self-consistent solution of the Poisson equation coupled with the Schrödinger equation as described earlier [38]. This gives an electrostatic potential profile which has large gradients near the interface and almost zero gradient in the middle of the molecule. Using such a potential profile, we also calculate the transport properties. However, the main results are found to be qualitatively similar to that obtained by using the ramp potential. Unless specified, all the current computations are presented using the ramp potential.

3. Results and discussions

3.1. Effect of dimerization in the low-bias regime

It is well known that a half-filled one-dimensional chain undergoes distortions due to dimerization. In our earlier work on SSH dimerized systems [14], we identified a critical bias V_c at which the frontier levels (HOMO and LUMO) come close to each other, resulting in a sharp rise and fall in current indicative of negative differential resistance (NDR). Since most of the molecular electronics materials are organic π -conjugated (alternating bond length) systems, here we try to understand microscopically the role of π -conjugation (dimerization) and the

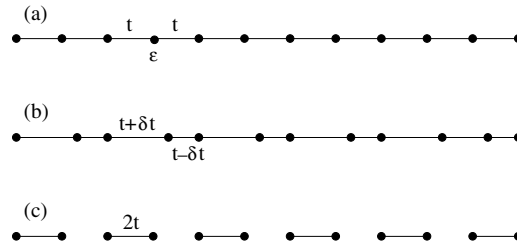


Figure 1. A molecular wire of N sites with (a) $\delta t = 0$, (b) $0 < \delta t < 1$, (c) $\delta t = 1$.

dependence of V_c on this parameter, through analytical expressions obtained considering the external bias as a perturbation. Due to conjugation, the ground state of such a system is a spin-density-wave insulator. Since the low-energy physics of carbon is purely due to π electrons, we consider a chain of N atoms with one electron per atom. This corresponds to the half-filled situation.

We first describe the situation for the completely dimerized chain (figure 1(c)). It specifies a system of $N/2$ isolated dimers with dimer hopping integrals $2t$. In the absence of bias, all the states are localized with the energy values $E^{(0)} = \pm 2t$, i.e., $N/2$ states have energy $E = 2t$, and the other $N/2$ have energy $E = -2t$. The application of an external bias V lifts this degeneracy. The energy expression of the system in the presence of a ramp potential, $V_n = -\frac{nV}{N+1}$, where n is the site index, can be written as

$$E_{\pm} = -\frac{(4m-1)V}{2(N+1)} \pm \frac{\sqrt{V^2 + 16t^2(N+1)^2}}{2(N+1)} \quad (3)$$

where $m = 1, 2, \dots, N/2$ is the dimer index, i.e. the m th dimer contains the $n-1$ th and n th site. More specifically, $m = 1$ denotes the first dimer with site labels 1 and 2 and $m = N/2$, the last dimer with sites $N-1$ and N .

From equation (3), it is clear that each of the energy level has a contribution from a particular dimer. It is easy to see that with the application of bias, the low-energy states, namely the HOMO and LUMO levels, have contributions from the first and the last dimer respectively. Equation (3) is plotted in figure 2. Since the slope of the levels increases with increasing dimer index, it is evident that the levels corresponding to the first and the last dimer (HOMO and LUMO levels) will meet for a certain value of V . Using equation (3) we calculate this critical value of the bias, V_c , as

$$V_c = \pm \frac{4t(N+1)}{\sqrt{(N-3)(N-1)}}.$$

This relation also indicates that HOMO and LUMO levels will meet at a lower value of V_c if we increase the system size.

We now consider a uniform chain ($\delta t = 0$) of N (even) identical sites. The chain is open and we do not consider the spin-polarization effects here (figure 1(a)). The Hamiltonian for the system in the presence of an external ramp potential adds a term,

$$H_1 = -\sum_{i=1}^N \frac{ieV}{N+1} a_i^\dagger a_i,$$

to the Hamiltonian H of the system. Using the perturbation theory, we calculate the ground-state energy, corrected up to the second order due to applied bias,

$$E_{N/2} = E_{N/2}^{(0)} + E_{N/2}^{(1)} + E_{N/2}^{(2)}, \quad (4)$$

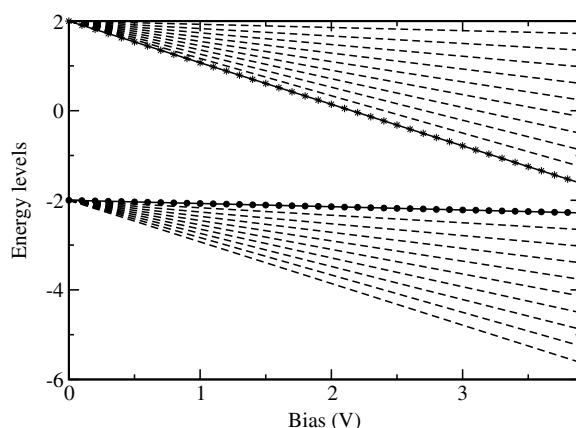


Figure 2. The variation of the energy levels of the perfectly dimerized system with external ramp bias ($t = 1$ and $\delta t = 1$).

where $E_{N/2}$ corresponds to the HOMO energy of the system. $E_{N/2}^{(0)} = 2t \cos(\frac{N\pi}{2(N+1)})$ represents the unperturbed ground-state energy. The unperturbed ground-state wavefunction is written as

$$\psi_{N/2}^{(0)} = \sqrt{\frac{2}{N+1}} \sum_{i=1}^N \sin\left(\frac{N\pi i}{2(N+1)}\right). \quad (5)$$

The first-order correction, from standard perturbation theory, yields

$$E_{N/2}^{(1)} = -\frac{2eV}{(N+1)^2} \sum_{i=1}^N i \sin^2\left(\frac{iN\pi}{2(N+1)}\right) \quad (6)$$

and the second-order correction due to the other states is

$$E_{N/2}^{(2)} = \sum_l \left[\frac{2e^2 V^2 \sum_{i=1}^N i^2 \sin^2\left(\frac{i\pi N}{2(N+1)}\right) \sin^2\left(\frac{i(N+2l)\pi}{2(N+1)}\right)}{(N+1)^4 [\cos(\frac{N\pi}{2(N+1)}) - \cos(\frac{(N+2l)\pi}{2(N+1)})]} \right]. \quad (7)$$

The index l is a positive integer such that $N/2 + l$ represents the l th one-electron excited state of the system. For example, the lowest unoccupied molecular orbital (LUMO) corresponds to $l = 1$.

As can be seen from the unperturbed wavefunction, every alternate energy level has exactly opposite parity. A perturbing external ramp potential with a linear spatial dependence will, however, destroy this parity symmetry. In the limit of large system size, the contribution to the first-order change in energy is zero, but the second-order perturbed term gives rise to non-zero contributions to the ground-state energy when the ground state mixes with states of opposite parity. Therefore, the ground state will have non-zero contributions only when the external bias mixes the HOMO with the LUMO, LUMO + 2, LUMO + 4, etc levels.

The slope of the HOMO energy calculated for the second-order change in the ground-state energy yields

$$\begin{aligned} \frac{dE_{N/2}^{(2)}}{dV} &= 4e^2 V \sum_l \frac{\sum_{i=1}^N i^2 \sin^2\left(\frac{i\pi N}{2(N+1)}\right) \sin^2\left(\frac{i(N+2l)\pi}{2(N+1)}\right)}{(N+1)^4 [\cos(\frac{N\pi}{2(N+1)}) - \cos(\frac{(N+2l)\pi}{2(N+1)})]} \\ &= -C(N, l)V \end{aligned} \quad (8)$$

where $C(N, l)$ is a positive constant for a fixed N and l . The negative sign appears because the ground-state energy is the lowest energy state of the system, and makes the denominator always negative. The slope of the ground-state energy then becomes

$$\frac{dE_{N/2}}{dV} = -C(N, l)V. \quad (9)$$

It is clearly evident from the above equation that the HOMO energy reduces with external bias and is thereby stabilized by the presence of an external electric field.

Now we introduce a partial dimerization in the chain (figure 1(b)). The chain has N identical sites with two different hopping integrals $t_1 = t + \delta t$ and $t_2 = t - \delta t$ for two successive bonds. The ground-state energy of the system is given by

$$E_{N/2}^{(0)} = \pm \sqrt{(t_1 - t_2)^2 + 4t_1 t_2 \cos^2\left(\frac{N\pi}{2(N+1)}\right)}$$

and the ground-state wavefunction is written as

$$\begin{aligned} \psi_{N/2}^{(0)} = & \sqrt{\frac{2}{N+1}} \sum_{n=0}^{N/2} \frac{t_1 e^{i\frac{N\pi}{2(N+1)}} + t_2 e^{-i\frac{N\pi}{2(N+1)}}}{E_{N/2}^{(0)}} \\ & \times \sin\left(\frac{N\pi}{2(N+1)} 2n\right) + \sin\left(\frac{N\pi}{2(N+1)} 2n+1\right). \end{aligned} \quad (10)$$

It is evident from the energy expression that the system has a large zero-bias gap and is thus insulating. The application of an external ramp bias gives a first-order correction to the HOMO energy level with an additional contribution as compared to that of the uniform chain, due to the mixing of the wavefunction coefficients between the sites of the each dimer. But in the large chain limit, as mentioned before, external bias which is an odd parity function results in a zero first-order correction to the energy. On the other hand, the second-order correction, after lengthy algebra, yields two kinds of term: one is similar to that of the uniform chain, except that it is modified by a larger energy gap in the denominator owing to the dimerized insulating nature of the system. This is the major contribution to the slope of the energy levels, which in this case is smaller compared to the uniform chain. The additional terms have a form

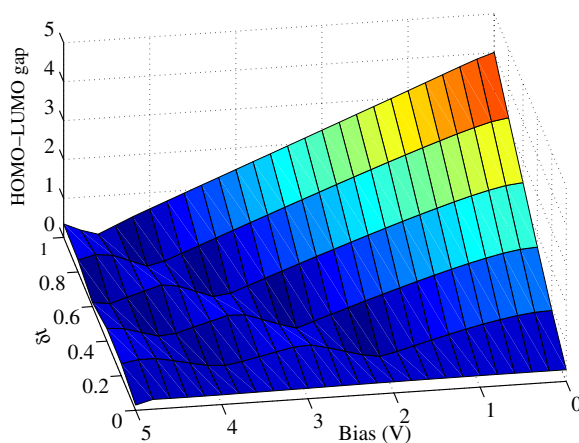


Figure 3. Variation of the gap between HOMO and LUMO energy levels with dimerization δt and the applied bias V as well.

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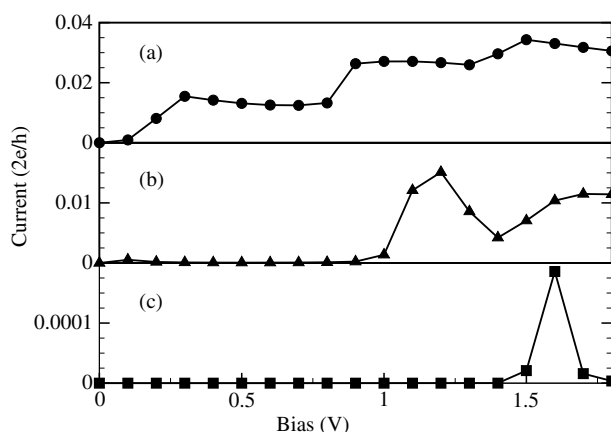


Figure 4. The I - V characteristics of a 20-site molecular chain with different values of δt (a) $\delta t = 0.05$, (b) $\delta t = 0.25$, (c) $\delta t = 0.5$, calculated at zero temperature.

dependent on the fourth power of the sin function and on second power of the bond-alternation parameter δt , and hence contribute very negligibly to the change in energies.

Since the slope in this case is smaller, it is clear that, for the partially dimerized system, there is a finite probability for the HOMO to meet the LUMO at some critical value of the external bias. Also, since the dependence of δt is in the second order, the variation of the slope of the energy levels for different δt is very small, although the initial gap is larger for larger δt . Interestingly, since the ground state consists of different contributions from two sites of a dimer, the bias intermixes them to create a dipolar contribution which essentially allows the low-energy levels to approach each other.

To summarize our findings on the behaviour of the low-energy states, in figure 3 we present the variation of the gap between HOMO and LUMO energy levels for a range of dimerization parameters (δt) and applied bias (V) for a system size $N = 40$. As can be seen, for the $\delta t = 0$ case, the gap is almost the same for all values of bias. However, for finite δt , $0 < \delta t < 1$, the gap is maximum at $V = 0$ and it decreases with increase in the bias value. After a critical value of V (V_c), it starts to increase again. It can also be seen that V_c shifts to a larger value with increasing value of the dimerization, δt , since the initial gap itself is larger for larger δt . In the experimentally observed NDR on Tour molecules with NO_2 and NH_2 substituents and with various end-groups, the critical bias has been obtained in the range of 2.0–3.5 V [39]. Our model system, although not directly comparable to these molecules, indicates dimerization strength of the order of 0.2–0.3 in order to obtain critical bias in this range. These are known to be very reasonable values for conjugated systems, with various substituents. Also, the sharpness of the peak at V_c is determined by the gap between the frontier levels at the critical bias, which is again related to the effective hopping integral for the system at that bias [14].

Since the low-energy behaviour of the chain with and without dimerization shows a drastic difference as a function of bias value, we expect such a difference to be reflected in the I - V characteristics as well. For a chain of $N = 20$, we have plotted in figure 4 the current–voltage characteristics for three representative values of δt . First, the current is drastically reduced with increasing value of δt owing to the strongly dimerized, insulating nature of the system. As can be seen, when the value of the bond-alternation parameter is very small, the I - V characteristics show nearly step-like behaviour but with slight reduction in current at a large value of bias. With increase in the value of the δt , gradually a sharp NDR peak appears at a critical bias V_c ,

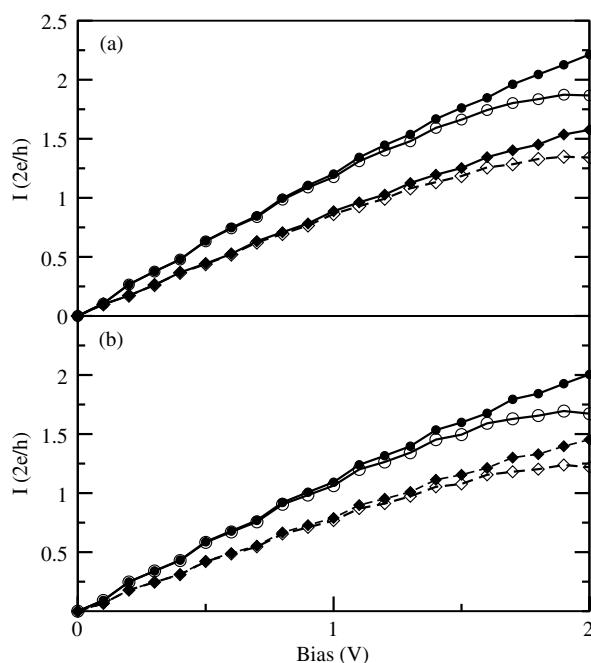


Figure 5. Current–voltage profile of a perfect chain connected between two (a) nickel and (b) cobalt electrodes. The number of sites N is 40 and the nearest-neighbour hopping integral is t . Circles and diamonds represent the parallel and antiparallel configurations respectively. The filled symbols represent the I – V characteristics of the system with the ramp potential and the unfilled symbols represent the I – V characteristics of the system with SCF potential.

as found in many Tour molecules [6]. For a strongly dimerized system, however, V_c shifts towards higher values of bias, as anticipated from the discussions above.

3.2. Effect of spin polarization

Now we consider that the molecular chain is connected to two polarized ferromagnets of same the material on either side. Due to magnetic polarizations, the electrodes have different charge densities for the up and down spin electrons. We calculate the current for the electrode–wire–electrode system due to the parallel and antiparallel orientations of the spins at the two electrodes separately. The broadening of the energy levels of the wire due to its interaction with the electrodes is given by $\Gamma_{L(R)} = 2\Delta_{L(R)}$, where $\Delta_{L(R)}$ is a measure of the spectral densities of the left (right) electrodes. We use $\Delta_{L(R)} = \pi\beta^2\rho_{L(R)}$, where β is the coupling between wire and the electrodes and $\rho_{L(R)}$ is the spin density of the left (right) electrodes. The electrodes considered are polarized Ni and Co substances. The up and down spin densities for nickel are 0.1897 and 1.7261 respectively, and those for cobalt are 0.1740 and 0.7349 respectively [15].

In figures 5(a) and (b) we have plotted the current (I) as a function of bias (V) for a perfect chain ($\delta t = 0$) attached to two different (Ni and Co) electrodes [15]. It is clear that the current due to the parallel spin configuration is always higher than that of the antiparallel configuration, especially at higher bias. This is expected of such molecular conductors which have negligible spin–orbit coupling and thereby no spin-breaking terms in the molecular wire. The current is also higher for Ni electrodes as compared to the current obtained for the same attached to Co electrodes. This is because the magnitude of the current in the wire depends on the extent of

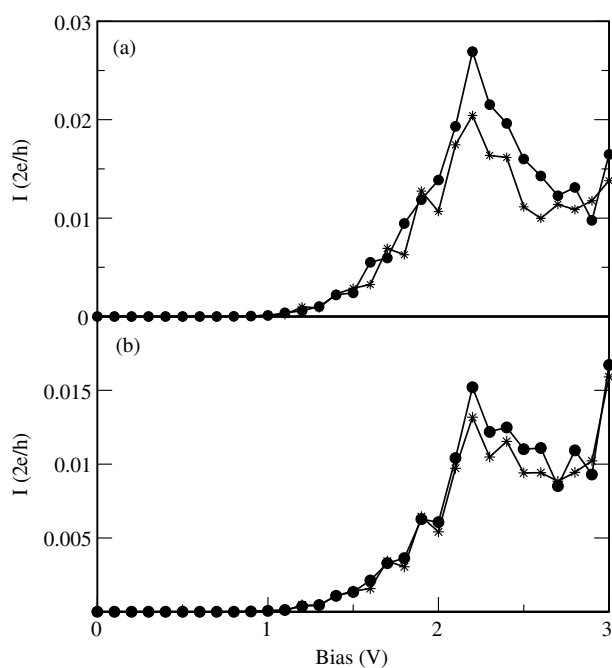


Figure 6. Current–voltage profile of a dimerized wire connected between two (a) nickel and (b) cobalt electrodes. $N = 40$, and the hopping integrals are $t + \delta t$ and $t - \delta t$, where $t = 1$ and $\delta t = 0.25$. Circles and stars represent the parallel and antiparallel configurations respectively.

broadening induced by the electrodes. Since the broadening is determined by the spin densities at the electrodes, which in the case of cobalt are smaller than that at the nickel electrodes, the magnitude of current is also reduced. Currents in these systems in the presence of a self-consistent field (SCF) potential (also shown in figure 5) have also been calculated. The results do not show any drastic qualitative change, over a range of bias.

Now we introduce dimerization in the chain such that there are two hopping integrals $t_1 = t + \delta t$ and $t_2 = t - \delta t$ arranged in an alternate way (figure 1(b)). We find that the current decreases drastically from its value obtained for a perfect chain and shows negative differential resistance (NDR) (figure 6). This is expected as the system is insulating and subject to lowering of gap with increase in bias as discussed above. The NDR peaks corresponding to parallel and antiparallel spin orientations, however, shift away from each other. Interestingly, the difference between the NDR peaks obtained for the two different spin orientations is higher for the Ni electrodes compared to the case with Co electrodes. The shift is due to the larger difference in the up and down spin densities for the Ni electrodes as compared to the Co electrodes. Also, an overall reduction in current has been found when two Co electrodes are attached to the wire. There has been much discussion in the literature on molecular spin-valve effects. Although experimental verification lacks proper reproducibility, recent reports of magnetoresistance effects in organic systems, namely, in octanethiol and in Alq_3 , show promises for future spintronic devices [28, 30].

To make a connection with the existing results, we also study the variation of the difference between current with parallel and antiparallel spin configurations with various degrees of dimerization (figure 7) for the molecule between both Ni and Co electrodes. The spin-valve effect can be clearly seen; however, this effect depends on bias itself: for a lower bias we get a

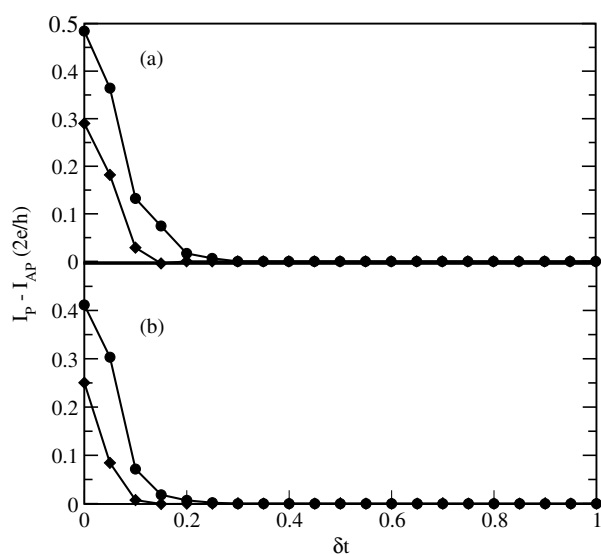


Figure 7. Variation of the difference between current with parallel and antiparallel spin configurations with various degrees of dimerization for (a) Ni and (b) Co. The line with filled circles represents $V = 2.2$ V and the line with diamonds represents $V = 0.8$ V.

lower magnetoresistance. Moreover, for a fixed value of V , the difference between the parallel and antiparallel current decreases with increasing δt , and after a certain critical value of δt it becomes almost zero. The critical δt values are identified to be 0.3 and 0.2 for Ni and Co electrodes respectively. This observation indicates that the dimerized system would lose its spin-valve characteristics for higher values of δt . The fact that the magnitude of every channel process (whether up or down spins) diminishes drastically due to the localized nature of the low-energy states of a system with high degree of dimerization, thereby destroying the spin-valve effect, is clearly evident from our picture. Such would also be the case for saturated systems between spin-polarized electrodes which also have highly localized frontier orbitals. In fact, these findings are corroborated by the results of Petta *et al* [28], who report magnetoresistance of 16% in a saturated system like octanethiol between Ni electrodes, which is much smaller than the giant magnetoresistance of 40% observed in a conjugated molecule like Alq₃ [30]. Moreover, theoretical calculations by Rocha *et al* [34] indicate large magnetoresistance in a tricene molecule, which is delocalized as compared to octanethiol (zero delocalization) between Ni electrodes. So, the very fact that both the saturated carbon system and the highly dimerized chain, although chemically very different, have localized low-energy states (strongly insulating behaviour) make both of them unsuitable for efficient spin-valve devices. Additionally, from our calculations, it can be seen that the difference in parallel and antiparallel current is larger for Ni electrodes as compared to Co, indicating that when the difference in the spin densities between the two electrodes is less, the spin-valve behaviour can easily be destroyed.

4. Conclusion

We have studied the effect of dimerization on the molecular energy levels of a single molecule attached to electrodes. We have analytically obtained the energies, slopes and the critical bias for three limiting cases: (a) $\delta t = 0$, (b) $0 < \delta t < 1$ and (c) $\delta t = 1$, in the presence of a small external bias. We find that the second-order correction to the ground-state energies caused by

the presence of a spatially varying bias results in a mixing of the frontier levels leading to a state conducive to showing NDR behaviour. We also observe that the critical bias at which NDR occurs shifts to higher bias with increase in the dimerization in the system.

We have also looked at the role played by the dimerization in the nature of spin-polarized current through the system. We find that the NDR peaks appear in the dimerized system as opposed to the perfect chain in both parallel and antiparallel orientations of the electrodes. But the spin-valve effect, which is characteristic of efficient spintronic devices, is destroyed in the presence of strong dimerization. This suggests that polyenes should show better spin-valve characteristics as compared to polyynes or saturated organic systems. Also, we find that, for a given molecule, electrodes with higher difference in their relative up and down spin densities (like Ni) would show better spin-valve behaviour, thus making them better electrodes for spintronic devices as compared to Co electrodes.

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