Investigation Electrical and Thermoelectrical properties of Ferrocene in staggered and eclipsed conformations

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Abstract: We present a comparative theoretical study of the electronic and thermoelectric properties of staggered and eclipsed ferrocene sandwiched between gold electrodes. These molecular junctions have been explored in two different configuration trans and cis conformation. In this work, we investigate the spin properties, in addition to thermoelectrical properties for all cases. Our results show that there is a variation in spin properties in staggered ferrocene when move from trans to cis configuration. However, in eclipsed ferrocene case there is no spin effects. Moreover, the room temperature electrical conductance in cis staggered ferrocene case is higher than other cases near the DFT Fermi energy. Furthermore, the thermopower of these junctions are rather high ranging about 150 µV/K. However, the thermoelectric figure of merit ZT of staggered ferrocene in cis configuration has the highest value with 1.06.

Keywords: Molecular junction, Quantum transport, electrical conductance, Seebeck coefficients, figure of merit

1. Introduction

Recently, huge interest and great efforts have been done in order to find and design thermoelectric materials which have the ability to convert wasted heat to electrical energy [1-6]. The thermoelectric figure of merit (ZT) is utilized to determine the efficiency of thermoelectrical materials and is given by \(ZT=S^2GT/\kappa\), where S is the thermopower or Seebeck coefficient, G is the electrical conductance, T is the temperature and \(\kappa\) is the electronic thermal conductivity [7-10]. Among several potential organic molecular ferrocene and its derivatives have attracted big attention due to their fundamental physical-chemical properties such as good thermal and chemical stability and its highest HOMO level[11].

Ferrocene Fe(C₅H₅)₂ is one of the most common broader classes of 3d, the structure of metallocene consists of two cyclopentadienyl (Cp) rings connected by a central metal atom[12]. Ferrocene was discovered in 1951, and it was the first example of a metallocene [13-16]. Since ferrocene’s appearances and because of its advantageous properties, that make it one of the most important candidates for various research applications, e.g. for the development of carbon nanotubes by pyrolysis[17] or for the creation of iron-oxide nanostructures[18]. The two ferrocene Cp rings display two distinct conformations where these two cyclopentadienyl rings can be in a staggered or eclipsed conformation and rotate around the low resistance Cp-Fe-Cp axis as shown in Fig.1a.[19-21]. However, the energy barrier for rotation of the ferrocene rings is very weak and therefore, they may
rotate freely and fast around symmetry axis, allowing both staggered and eclipsed forms to be observed.[22-26]

In this paper, our study focusing on two main aspects. The first one is to investigate the spin state therefore, all the calculations are spin-polarized where the total transmission is the summation of spin up and spin down. The second aspect is to investigate the electrical and thermoelectrical properties of ferrocene with staggered and eclipsed conformation in two different configurations trans and cis between a pair of gold nanoelectrodes as shown in Figure 1.b, and c.

2. Method

Firstly, the geometry of each isolated molecule was optimized. Then in the vicinity of gold electrodes the geometry of each contact was optimized again, the thiol anchor group was used to bind ferrocene units to gold leads as shown in Figure 1b and c. We used the spin density functional theory (DFT) code SIESTA[28], with a double-ζ polarized basis set (DZP) [29] and generalized gradient functional approximation (GGA-PBE) [30-31]. When we obtain the Hamiltonian H then combined this Hamiltonian with the transport code, GOLLUM[27] to calculate the transmission coefficient $T(E)$. The electrical conductance was computed by using Landauer formula. We compute the thermopower $S$ over a wide range of Fermi energies by using equation $S = -\frac{1}{eT} \frac{L_1}{L_2}$ where $T$ is the temperature, $e$ is
electron charge and Ln can be calculated as \( L_n = \int_{-\infty}^{\infty} \left( E - E_F \right)^n T(E) \left( \frac{\partial f(E,T)}{\partial E} \right) \ dE \) where \( f(E,T) \) is the Fermi-Dirac probability distribution function[9].

3. Results and discussion

The calculated spin-polarized transmission functions of the two ferrocene molecular conformations staggered and eclipsed with two different configurations trans and cis against the energy are shown in Figure 2. For staggered conformation in trans configuration Figure 2.a shows that a significant difference is observed between spin up (red line) and spin down (black dotted line) and the transmission in the spin down is higher than spin up particularly around Fermi energy \( E_F = 0 \). While in cis configurations there are no discernible differences in transmission functions where spin up and spin down are identical as shown in Figure 2.b. Figure 2 shows the spin-dependent transmission for the eclipsed case with trans (Figure 2.c) and cis case (Figure 2.d). As we can see in these figures the transmission curves for the trans and cis configurations possessing almost identical transmission curves. This confirming that there are no spin affects in eclipsed conformation in both trans and cis cases.

**Figure 2.** Shows the spin dependent transmission coefficient of staggered ferrocene in (a) trans and (b) cis,
Figure 3. Shows the spin dependent transmission coefficient of eclipsed ferrocene in (c) trans and (d) cis.

Figure 3. illustrate the corresponding conductance in staggered and eclipsed configurations for trans (Figure 3.a) and cis (Figure 3.b) cases. From these figures, it is apparent that in both cases the electrical conductance in cis configuration (red line) is higher than trans one around Fermi energy $E_F=0$ eV.

Figure 4. shows the electrical conductance as a function of energy for ferrocene in (a) staggered, and (b) eclipsed.

Figure 4.a and b show the results for the (thermopower) S for staggered and eclipsed cases in both trans, and cis configurations. Figure 4.a and b demonstrate that both the magnitude and sign of Seebeck coefficient S are sensitive to the structure conformation. The electronic thermal conductance of these junctions is shown in Figure 4.c and d. However, these figures show that the values of electronic thermal conductance of cis configuration are slightly higher than that of the trans near the Fermi energy in both staggered and eclipsed cases.
The essential quantity that determines the efficiency of a thermo-electric material or device is the room temperature figure of merit $ZT$. Figure 5 shows that the value of figure of the merits $ZT$ of staggered (Figure 5a) and eclipsed (Figure 5b) in trans and cis configurations. Figure 5a, b show that the cis conformation in both staggered and eclipsed cases has a higher value of $ZT$ ranging between 0.255 to 1.06.

Figure 5. Show (a,b) Seebeck coefficient $S$ and (c,d) the electronic thermal conductance for staggered and eclipsed ferrocene in trans and cis configurations.
On the basis of the above results, and to make the comparison more clear all the thermoelectric properties of ferrocene (staggered and eclipsed) in trans and cis configuration have been combined together in Figure 6. This figure shows the comparison of electrical conductance, thermopower, and figure of merit for all cases. Figure 6a shows that the staggered ferrocene in cis configuration has the highest value of electrical conductance around Fermi level. In addition to high electrical conductance, staggered ferrocene in cis configuration also shows the highest value of thermopower at the Fermi level as shown in Figure 6b. According to these transport properties, a figure of merit $ZT$ of staggered ferrocene in cis configuration shows the highest figure of merit $ZT \approx 1.066$ as shown in Figure 6c.

Figure 7. shows (a) electrical conductance and (b) S (thermopower) for staggered and eclipsed ferrocene in trans and cis configurations.
In this work, we introduce a comparison study of the electrical and thermoelectric properties of ferrocene molecules in staggered and eclipse conformations. We proved that the spin-dependent transport properties and thermal conductance is affected significantly by the variation of configuration from staggered to eclipse. Our results demonstrate that staggered ferrocene in cis configuration is the attractive configuration for molecular-scale thermoelectricity, and that because of the large values of the electrical conductance and the Seebeck coefficient leading to a promising value of figure of merit.

5. References

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ACKNOWLEDGMENTS
The authors introduce their great thank and acknowledge to Prof. Lambert for enabling the calculation of this work to be carried out in his laboratory.