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Charge-induced spin polarization in thiophene oligomers

Dong Hou, Junjie Qiu, Shijie Xie and Avadh Saxena

1 School of Physics, National Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, People’s Republic of China
2 Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA
E-mail: houdong@ustc.edu.cn and xsj@sdu.edu.cn

Abstract. Charge-induced spin polarization in small organic molecules is a key factor for spin transport and magnetic effects in related organic devices. In this work, we study spin polarization in charged thiophene oligomer molecules by calculating the magnetic moment with density functional theory. It is found that the emergence and variation of the net magnetic moment is related to both the amount of charge injected and the polymerization of the oligomer. In combination with model analysis, we conclude that the strong electron–electron interaction and electron–lattice interaction in organic materials are responsible for charge-induced spin polarization.
1. Introduction

Organic semiconductors (OSCs) refer to a large variety of organic molecules or polymers that have abundant functional properties related to electricity, magnetism and optics. OSCs have caught the attention of the spintronics community and significant efforts are being made toward their integration in this field. One attractive aspect of organic spintronics is the weakness of the spin-scattering mechanism, implying that the spin polarization of the carriers can be maintained for a relatively very long time. Spin-relaxation time in OSCs may be as long as 10 µs, which exceeds the characteristic time in inorganic materials by orders of magnitude [1]. Owing to the softness and ease of operating with organic materials as well as the possibility to chemically tailor specific functionalities, there is a huge potential for the development of versatile, low-cost organic electronic and spintronic devices [2, 3].

The electronic properties of OSCs are radically different from those of normal inorganic semiconductors such as Si or GaAs with rigid band structures. In band semiconductors, the spin injection and transport are usually described by considering either ballistic or diffusive motion of spin-polarized carriers, electrons or holes with spin-half, in extended band states. The spin-polarized state and its attendant spin-flipping processes occur mainly via spin–orbit interaction. OSCs are neither characterized by band conductivity nor do they possess a significant spin–orbit interaction. The carriers in OSCs are localized in space, called polaron or bipolaron. A polaron has one electronic charge with spin-half, while a bipolaron has two electronic charges with no net spin moment. They propagate by incoherent hopping between strongly localized states.

A key issue in organic spintronics is the realization of spin-polarized electrical injection and transport in the organic layer. It appears that OSCs are comparably well suited for spintronic applications. In particular, the π-conjugated sexithiophene (T₆, one kind of thiophene oligomer) thin films and tris(8-hydroxy-quinoline) aluminum (Alq₃) have been discovered to perform very well as organic spin valves or exhibit magnetoresistance, providing one of the best giant magnetoresistance values. For example, Dediu et al [4] carried out the first spin transport experiment in LSMO(LaₓSr₁−ₓMnO₃)/T₆/LSMO which were followed by Xiong et al’s [5] experiments in LSMO/Alq₃/Co. They all observed the injection, transport and detection of spin-polarized carriers in the OSCs. In 2003, Kalinowski et al [6] found a change of 2% in the resistance of Alq₃ for an applied magnetic field of 0.5 T. This anomalously large magnetoresistance, which appears at room temperature and weak magnetic fields (as small as 50 mT), has also been observed in the thiophene oligomer and some conjugated polymers [7–9]. Interestingly, in these devices neither magnetic leads nor magnetic molecules are included. It implies that spin-degenerate charge injection can also possibly induce spin-polarized states in OSCs, which could respond to the applied weak magnetic field.
Among all the functional organic molecules, thiophene oligomer and Alq$_3$ are relatively well known and have been widely used as components in organic spintronic devices. However, up to now, it is not understood precisely why thiophene oligomer or Alq$_3$ give rise to extremely long spin-relaxation times [10], to a high giant magnetoresistance [5] and significant tunnel magnetoresistance values [11]. In 2003, we theoretically studied the injection of electrons (holes) from a conventional ferromagnetic metal or a half-metallic ferromagnetic colossal magnetoresistance manganite electrode into a polymer layer [12] and found that there can be spin density polarization in the polymer near the interface. The spin density oscillates and decays into the polymer with a decay length of about six times the lattice constant of the polymer. Later in 2006, we studied the dynamic process of charge injection from a metal electrode into an organic layer within the framework of a non-adiabatic approach. It was found that the injected charges form wave packets due to the strong electron–lattice (e–l) interaction in the organic layer. A wave packet may contain any amount of charge up to two electronic units, which depends on the injection condition. As the system is spin degenerate within the model, a wave packet has zero spin moment [13].

In 2010, Tarafder et al [14] considered this question by calculating the spin polarization of injected charges in the Alq$_3$ molecule using density functional theory (DFT). They found that spin-degenerate charge injection could induce a net spin moment which increased linearly with the amount of charge injected into Alq$_3$. They attributed the emergence of a net magnetic moment to charge-induced structural distortion, so that the electron occupation of $p_z$ orbital was different in different nitrogen atoms. We notice that in their work there is a puzzling over-saturation of spin polarization, meaning that the induced total magnetization $M$ is larger than that provided by the injected charge $q$ ($M > q\mu_B$, charge is in units of electronic charge $e$). Besides, Alq$_3$ contains a metal atom with a relatively uniform structure, lacking the various deformations characteristic of organic molecules, e.g. thiophene oligomer. All these factors make it difficult to elucidate the reason for charge-induced magnetism in Alq$_3$.

Therefore, it is necessary to investigate charge-induced magnetism in a pure organic material such as thiophene oligomer. A thiophene molecule has a planar five-member heterocyclic structure composed of carbon and sulfur atoms. It has been extensively studied in organic chemistry since thiophene oligomer was first synthesized about 70 years ago [15]. Later investigations showed that end-capped thiophene oligomers with various polymerization numbers, for example from 2 to 10, could be synthesized [16, 17]. After simple chemical modification, positively or negatively charged thiophene oligomers could be directly characterized in solution by spectroscopic techniques [18, 19]. Concerning the charge injection, most research interests have been focused on singly or doubly charged thiophene oligomers both experimentally [20, 21] and theoretically [22, 23]. However, to the best of our knowledge, there is no clear information about the magnetization or spin polarization of charged thiophene, and what the relation is between magnetization and the injected charge amount, as well as the effect of thiophene polymerization. More importantly, the physical mechanism for the emergence of the magnetization is still unrevealed.

In this work, using DFT calculations together with model analysis, we try to resolve the above issues by systematically investigating the spin polarization in a set of thiophene oligomer molecules $T_n$ ($n$ is the number of polymerized thiophene molecules). The effect of molecular size on the spin polarization is studied by considering the polymerization of thiophene rings. Through a tight-binding model, we analyze the origin of spin polarization of a given charged
molecule. We reveal that the strong e–l interaction in organic molecules is the key factor for the appearance of spin polarization of the injected charges.

2. Computational methods

The first principle calculations are performed by DFT implemented in the Siesta code [24]. The Perdew–Burke–Ernzerhof exchange-correlation functional within the generalized gradient approximation is adopted [25]. The basis sets for all atoms are all double-$\zeta$ plus polarization functions, and the mesh cutoff is 400 Ryd. The total energy is converged until the criterion of $10^{-5}$ eV is reached.

In this work, we consider thiophene oligomers from 2-thiophene to 8-thiophene ($T_2$, $T_3$, . . . , $T_8$, respectively). For simplicity, these oligomers are terminated with hydrogen atoms at the end points. The molecule is placed into a very large simple cubic unit cell to avoid direct interactions between adjacent periodic images. In the charged molecules, their total energies are corrected by Madelung terms, and the initial injected charges are not assigned to have any net spin moments. The structures of neutral molecule $T_n^{(0)}$ and charge-injected molecule $T_n^{(q)}$ are all fully relaxed to ensure that the force on each atom is smaller than 0.01 eV Å$^{-1}$.

3. Results and discussions

The structure of a pristine thiophene oligomer is calculated first. The results show that $T_n^{(0)}$ has a planar feature. $T_{2k+1}^{(0)}$ has a mirror symmetry, while $T_{2k}^{(0)}$ has a two-fold rotation symmetry. Then, the electron-charging states of $T_n^{(q)}$ molecule are calculated. It is found that they are still planar and keep their original symmetry unchanged. To analyze the spin polarization of a $T_n^{(q)}$ molecule, we define the magnetic moment on the $i$th carbon or sulfur atom of the molecule as $m_i = (q_{i,\uparrow} - q_{i,\downarrow})\mu_B$, in which $q_{i,s}$ is the total charge with spin $s$ on atom $i$. Here $\mu_B$ denotes the Bohr magnetron. Then the total magnetic moment of the molecule is $M = \sum_i m_i$.

Our DFT simulations show that the spin-polarized state is always energetically favorable to the non-polarized one. We calculate the total energy of a charged molecule with spin restriction or relaxation separately. Taking $T_6$ as an example, with extra charge of $q = 1.0e$, it is obtained that the energy of spin-polarized state is 33 meV lower than that of the non-polarized one. Figure 1 shows the total magnetic moment of molecules $T_n^{(q)}$ in the lowest energy state.

Some interesting results are found. (i) There is a minimum value $q_c$ of injected charges for the appearance of the spin-polarized state. For $T_6$, for example, the minimum value is $q_c \approx 0.3$. When the injected charge is less than $q_c$, the lowest energy state of the molecule is spin-degenerate with zero magnetic moment. When the injected charge is larger than $q_c$, a net magnetic moment emerges. The minimum polarization charge depends on the size of the thiophene oligomer or polymerization. For example, spin polarization appears when injected charge $q \geq q_c = 0.1$ in $T_2$ and $T_3$ molecules, while $q \geq q_c = 0.4$ in $T_8$. In [14], it seems that there is no minimum value of $q_c$ for Alq$_3$. In other words, $q_c = 0$ is deduced for the small molecule Alq$_3$. (ii) The behavior of charge-induced magnetic moment is related to the molecular size. As shown in figure 1, for small molecules $T_2$ and $T_3$, the magnetic moments increase nearly linearly with the injected charges. For large molecules $T_7$ and $T_8$, the tendency of the magnetic moments to increase becomes weak. For all the molecules, it is found that the magnetic moment reaches saturation when one electronic charge is doped, beyond which, the moment begins to decrease.
(iii) The magnitude of spin polarization decreases with increasing polymerization of molecules. With a certain amount of charge injected, the molecule with larger \( n \) always shows a smaller magnetic moment. As depicted in figure 2, when the injected charge \( q = 1.0e \), it is nearly fully spin polarized in \( T_2 \) with \( M \approx 1.0 \mu_B \). But in \( T_8 \), it is obtained that \( M \approx 0.7 \mu_B \), which shows that the charged \( T_8 \) is partially polarized. The situation is similar when \( q = 0.6e \).

These results on thiophene oligomers have two different features when comparing to the Alq\(_3\) molecule. One is the existence of a minimum polarization charge in thiophene oligomer molecules. The other is that there is no over-saturation phenomenon of spin polarization in thiophene oligomers, meaning that the total magnetic moment is always smaller than what can be provided by the injected charge.
To get a better physical understanding of the origin of the induced magnetic moments and the characteristic of charging property of thiophene oligomers, we consider a tight-binding Hamiltonian including the electron–electron (e–e) interaction

\[ H_{\text{Hubbard}} = - \sum_{i,s} t \left( c_{i,s}^\dagger c_{i+1,s} + c_{i+1,s}^\dagger c_{i,s} \right) + \sum_{i} U c_{i,\uparrow}^\dagger c_{i,\downarrow} c_{i,\downarrow}^\dagger c_{i,\uparrow}, \]  

(1)

where \( c_{i,s}^\dagger (c_{i,s}) \) is the creation (annihilation) operator of an electron at site \( i \) with spin \( s \), \( t \) is the electron hopping integral between neighboring sites and \( U \) is the e–e interaction on the same site. The first term of the Hamiltonian represents the electron hopping between adjacent sites, which requires equivalent spins to minimize the energy. The other term describes the e–e Coulomb repulsion on the same site, which favors spin-polarized distribution. Thus from this qualitative analysis, the emergence of magnetic moments is a result of the competition between the e–l coupling and the e–e Coulomb repulsive coupling, in which the amount of injected charge adjusts its relative strength. In band theory, a ferromagnetic state \( M \neq 0 \) will appear when \( U > U_c = 3/[2\rho(\bar{e}_\uparrow)] \) (Stoner criterion) [26]. It tells us that the appearance of a ferromagnetic state is closely related to the density of states, which depends on the Fermi level or electronic occupation.

Stoner criterion describes the behavior of extended states in an infinite system. But in the present case the organic molecule only contains a few or tens of atoms and strong e–l coupling, where the electronic states are highly localized. To understand it, we check the distribution of the magnetic moments on each five-membered ring of the molecule. As shown in figure 3, it is found that the moment distribution has the characteristic of localization when the moment appears. The moments on the inner rings are larger than those on the outer rings. From the charge distribution \( q_i = q_{i,\uparrow} + q_{i,\downarrow} \) we know that the injected charge will form a localized state called a polaron due to the strong e–l interaction [13] which has been observed in experiments [27, 28]. The localization of the moment is consistent with that of the charged polaron. As the e–e interaction energy will increase with the localization of the charge, the spin polarization of the charge will be favored and a net magnetic moment will appear.

Figure 3. Magnetic moment distributions on each five-membered ring of \( T_7 \).
Figure 4. Spatial distribution of the charge-induced magnetic moment in molecules from $T_2$ to $T_7$ ($q = 1.0e$). Note that for plotting convenience the isosurface values for each molecule are different.

Figure 4 gives the detailed magnetic moment distribution on each atom of a molecule with one electron injected. There exists an oscillation of the magnetic moment along the carbon chain. The end carbon atoms are always spin polarized. Going toward the central part of the molecule, the magnetic moment emerges on every other carbon atom. As the number of carbon atoms is even in the molecule, the moment distribution appears as a kink in the center of the molecule.

The relation between the magnetic moment and the localization of injected charge is further confirmed by the bond length distortion of the molecule. The C–C bond length variation $\Delta l_i = l_i^{(q)} - l_i^{(0)}$ for $T_7$ when $q = 0$ is shown in figure 5. The positive (negative) value in the upper panel of figure 5 represents bond stretching (shrinking). It is clear that C–C bonds in charged $T_7$ stretch and shrink alternately, which is called dimerization. It is also noted that the central part of the molecule has larger bond length distortion. Combined with the result in figure 3 that the induced magnetic moment concentrates in the central part of the molecule, it is natural to reach the conclusion that the formation of a localized polaron is the reason for charge-induced magnetism in organic molecules.
To further verify the importance of the localized defect, we fix the structure of a neutral molecule and calculate the total energy of a charged molecule. It is found that the non-magnetic state is energetically lower than the spin polarized one, which is opposite to the situation when the structure is fully relaxed. For example, if we fix the structure of $T_7$ to its relaxed neutral state and inject charge $q = 0.5e$, the total energy of the non-magnetic state is at least 6 meV lower than that of the spin-polarized state. However, if the structure relaxation is allowed, the total energy of the relaxed spin-polarized state is 50 meV lower than that of the non-magnetic state. This result proves that the structure relaxation or the charge localization induced by the e–l interaction is crucial for charge-induced spin polarization in thiophene oligomer molecules.

The charge-induced spin polarization in thiophene oligomers will dramatically influence the spin injection and transport behavior. For example, this makes it possible for thiophene oligomer devices to respond to an external magnetic field even in the absence of magnetic metals. When spin degenerate charges are injected into the thiophene layers, the strong e–l as well as e–e interactions generate localized spin-polarized polarons in thiophene molecule. Without an external magnetic field, the spin-up and spin-down components are equivalent so that these local magnetic moments orient randomly, leading to a cancelation of their contributions to spin-polarized transport. However, when an external magnetic field is applied, these local moments align accordingly to form a spin-polarized transport barrier. In this case the two spin components are no longer equivalent in the transport process, bringing about a spin-polarized current.

Moreover, our simulations reveal that the spin-polarized state is energetically favorable. It is expected that this state is stable even when we include the spin–orbit interaction as it has been indicated that the spin–orbit interaction is very weak in organic materials. To understand the large organic magnetoresistance (OMAR) effect, certain mechanisms, such as exciton, bipolaron and polaron–exciton mechanisms [29–31] have been proposed. All these mechanisms are intimately related to the spin characteristics of the injected charges. Therefore, our simulations support these mechanisms.

It should be noted that the spontaneous spin polarization of injected charges in organic molecules is distinct from that in their inorganic counterparts. Except for the large OMAR
mentioned above, some other phenomena may be different. For example, the Hanle effect [32] that has been widely used for the detection of spin injection and transport in inorganic semiconductors [33, 34] may appear different in OSCs. This effect has not been observed in OSCs yet, with its reason still being debated [35]. According to our calculation, in thiophene oligomers the injected charges are bound to the lattice degree of freedom via the strong e–l interaction. This fact makes the transport mechanism in OSCs to be the incoherent hopping of polarons that is totally different from the band transport in inorganic semiconductors. By forming a polaron, the spin-up and spin-down components with different amounts are strongly related by their interactions to the lattice, rendering the (possible) spin precession more complex and difficult. In addition, the hopping direction of polarons between adjacent molecules in disordered OSCs is not well defined. These intrinsic differences may be responsible for a lack of observation of the ‘Hanle effect’ in OSCs. Further investigations are needed to clearly explain this important issue.

4. Conclusions

Using first-principle DFT calculations, we investigated charge-induced spin polarization in thiophene oligomer molecules. We found that charge injection can induce a net magnetic moment in an organic molecule even if there are no magnetic metallic elements present in the molecule. The induced magnetic moment is related to both the amount of charge injected and the size of the molecule. We revealed the existence of a localized spin-polarized state at the center of the charged molecule, together with a structural distortion in this region. It indicates that the strong e–e interaction and e–l interaction in organic molecules are the main sources of charge-induced spin polarization.

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