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Density Functional Theory Calculations of Charge-Induced Spin Polarization in Pentacene

Jun-feng Ren*, Yan-ru Zhang, Xiao-bo Yuan, Gui-chao Hu

College of Physics and Electronics, Shandong Normal University, Ji'nan 250014, China

Based on density functional theory (DFT) calculations, we investigate the spin-related properties of spinless-hole injected organic molecule pentacene (Pc). DFT calculations reveal that there is spontaneous spin polarization in Pc when spinless-hole is injected. The charge-induced magnetic moment of Pc increases linearly with the increasing of the extra hole charge amount and its maximum can be up to 1 μ_B per injected spinless-hole per Pc molecule. The magnetic moment is expected due to the injected unpaired charge. The injected hole will preferably fill the spin-splitted carbon p_z orbitals, which makes the Pc molecule spin polarize.

Key words: Organic spintronics, Spontaneous spin polarization, Density functional theory, Pentacene

I. INTRODUCTION

Small molecule organic semiconductors, which contain hydrocarbons and their compounds doped with other atoms, have achieved many important applications due to their abundant functionalities [1−8]. The most popular and research interests on a large number of hydrocarbons are aromatic systems, such as naphthalene, anthracene, acene, and rubrene *etc*. As a traditional sample of hydrocarbon, pentacene (Pc) has high mobility and good crystalline quality, which make it be an optimal organic material for carrier transport [9, 10]. Pc has also been widely studied on surfaces of different materials [11−16]. For example, Ferretti *et al.* studied the adsorption properties of Pc on Cu experimentally and theoretically [11]. They demonstrated the electronic mixing between Pc orbitals and Cu electronic states. Jeong *et al.* investigated the microscopic mechanism of the dipole layer formation at the interface of Pc/Si(001) by first-principles calculations and photoelectron spectroscopy [12]. Based on the density functional theory (DFT) calculations and photoelectron spectroscopy, Müller *et al.* analyzed that adsorption mechanism in Pc/Cu(110) system was chemisorption [13, 14]. They predicted that there was charge redistribution at the interface and a significant bending of the Pc would happen. Mahns *et al.* investigated the electronic properties of Pc films using spectroscopic methods as well as DFT calculations [15]. Tanaka *et al.* demonstrated a direct determination of charge carrier concentration in the operating devices of Pc and poly(3-hexylthiophene) [16].

Pc was widely used in organic spintronic applications. Many experiments showed that spin polarized carriers could be transported in Pc, and magnetoresistance (MR) could be obtained in Pc-related organic spintronic devices [17−24]. Popinciuc *et al.* studied the energy level alignment and the electronic structure of the Co/Pc/Co interfaces [17]. Shimada *et al.* fabricated devices using Pc sandwiched between Co-doped TiO_2 and Fe [18], they found that the MR properties of the devices can be explained by the effect of the interface morphology and spin polarization of interface traps. To emulate the interfacial regimes, Chan *et al.* fabricated ultrathin Pc/Co and Co/Pc bilayers and found that the Co/Pc was chemically stable, whereas Pc/Co was reactive and exhibited complex magnetization pattern [19]. Wei *et al.* studied the magnetic configuration of an ultrathin Co film in contact with Pc layer and found that Pc absorption had different influence on the bottom and the top Co layers [20]. Hong *et al.* fabricated organic spin valves with the structure of NiFe/CoFe/Pc/CoFe, and they found that there was derivative oxide at the metal/organic interface, which was created by the plasma-induced modification. The derivative oxide acted as the insulating barrier at the interface and enhanced the MR in the organic spin valve [21]. Mooser *et al.* investigated room temperature spin polarized injection and transport in solution-processed 6,13-bis(triisopropylsilylethynyl)-Pc (TIPS-Pc) using vertical CoPt/TIPS-Pc/AlO_x/Co spin valve [22]. Alborghetti *et al.* investigated interdigitated lateral structures with Pc deposited between two electrodes [23]. They revealed that different electronic structures between metals and Pc do not benefit spin injection. Wang *et al.* demonstrated that the interfacial barrier between Pc and Co could be modified by inserting a MoO_3 buffer layer, and suggested that the MoO_3

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*Author to whom correspondence should be addressed. E-mail: renjf@sdnu.edu.cn

buffer layer could be used in p-type organic spintronic devices to reduce the interfacial barrier [24].

A Pc molecule is composed of only carbon and hydrogen atoms and no magnetic elements. Pc molecule is also highly symmetric in the molecular plane. This particular structure makes Pc different from other organic molecules discussed in the case of charge-induced spin polarization, such as Alq_3 and polythiophene [25−29]. For example, Tarafder *et al.* considered that an asymmetry of the Al−N bond lengths in Alq_3 molecule led to an asymmetric distribution of injected charge over the molecule and then the charged Alq_3 molecule was spin polarized [25]. However, a Alq_3 molecule contains a Al metal atom which makes it difficult to elucidate the reason for the charge induced magnetism. Exploring the impact of the high symmetry on the spontaneous spin polarization in spinless-hole injected Pc containing only carbon and hydrogen atoms will help us to elucidate the mechanism of charge-induced spin polarization in organic materials. In this work, for spinless-hole injected Pc, DFT calculations reveal the atomic arrangement of Pc, and spontaneous spin polarization in Pc with the maximum magnetic moment being 1 μ_B per injected spinless-hole per Pc. The mechanism of charge-induced spin polarization in Pc is also detailedly discussed.

II. COMPUTATIONAL METHODS

Pc molecule is put in a unit cell with the vacuum space about 20 Å to avoid interactions induced by periodic boundary conditions. VASP [30, 31] is used to perform the calculations. The exchange-correlation potential is considered by using Perdew-Burke-Ernzerhof generalized gradient approximation (GGA). The energy cutoff is set to be 550 eV in each calculation. The structural relaxations continue until the forces on each atom are less than 0.02 eV/Å. We first relax the isolated Pc molecule and get the ground state. To simulate the spinless-hole injection, we add extra spinless-hole charge q to this ground state and do relaxation again, and a uniform opposite background charge is used to neutralize the simulation cell. It should be noticed again that the added extra hole does not carry any spin. It is found from the calculations that the total energies for spin-polarized and non-spin-polarized calculations are the same for isolated Pc molecule. However, for spin-less hole injected Pc, it is found that spin-polarized state has lower total energy than that of non-spin-polarized state, so spin-polarized state is more stable and spin-less hole injected Pc is spin polarized.

III. RESULTS AND DISCUSSION

Relationship between Pc molecules magnetic moment and injected spinless-hole charge amount q is shown in Fig.1. It is clear that the magnetic moment of Pc
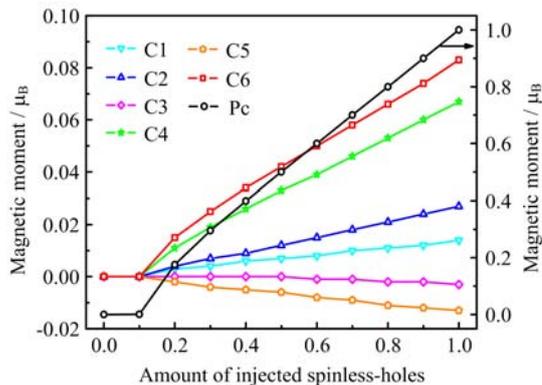
FIG. 1 Magnetic moment as a function of injected spinless-hole charge amount.

TABLE I Carbon-carbon bond lengths of ground-state Pc and one spinless-hole injected Pc, as well as the bond length changes between them (in Å).

	0 e	1 e	1 e−0 e
C1−C2	1.36919	1.37923	0.01004
C2−C3	1.43192	1.42190	−0.01002
C3−C4	1.39211	1.40340	0.01129
C4−C5	1.41352	1.40747	−0.00605
C5−C6	1.40382	1.40665	0.00283
C5−C7	1.45976	1.45591	−0.00385
C3−C8	1.45612	1.44986	−0.00626
C1−C9	1.42881	1.41678	−0.01203

is not zero when $q>0.1$, and then it increases linearly with the increasing of q, the maximum is about 1 μ_B. The injected hole does not carry any spin, although the magnetic moment of spinless-hole charged Pc is not zero, spinless-hole charge injection spontaneously spin polarizes normal nonmagnetic Pc. The reason of the net magnetic moment is induced by the injected unpaired carriers. There is no doubt that after spin-less hole injection in Pc, there will be coulomb interactions between the injected additional carriers and the carbon atoms, then the bond lengths will be changed compared with the isolated Pc, *i.e.*, the bond length change is another consequence of the injected charge carrier. Also different bond lengths change differently upon spin-less hole injection due to the different connections of particular carbon atoms. We have given some sample C−C bond lengths of ground-state Pc and one spinless-hole injected Pc, as well as the bond length changes between them, as shown in Table I. Although the Pc molecule is highly symmetric in the molecular plane, the C−C bond lengths are not equal even in the ground-state structure. Compared to the ground-state structure, in one spinless-hole injected Pc, the C1−C2, C3−C4, C5−C6 bond lengths are increased, however, other C−C bond lengths become reduced. Coulomb interactions between the injected additional carriers and the carbon atoms
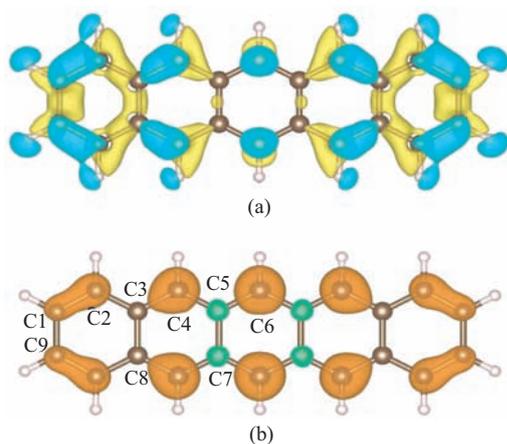
FIG. 2 (a) Charge density distribution of the injected hole is shown by the yellow-blue hyper surface. (b) Spin density distribution of one spinless-hole injected Pc is shown by the orange-green hyper surface. Carbon and hydrogen atoms are shown as brown and pink spheres, respectively. For interpretation of the color in this figure legend, the reader can refer to the web version of this article.

FIG. 3 The total DOS of the ground-state Pc and one spinless-hole injected Pc, respectively.

make the hole charge density redistribute within Pc, which is shown in Fig.2(a). And the spin density of one spinless-hole injected Pc is also not distributed equally over all atoms, which is shown in Fig.2(b). It is clear that the spin density resides predominantly on the C1, C2, C4, and C6 atoms.

We have also discussed the contributions of different carbon atoms to the magnetic moment, as shown in Fig.1. While the injected hole charge increases, the magnetic moments of C1, C2, C4, and C6 increase whereas those of C3 and C5 decrease. This different behavior corresponds to the different bond length changes induced by the injected unpaired charges. Particular carbon atoms in Pc have different neighbors. The three nearest neighbors of C3 and C5 are all carbon atoms, however, the three nearest neighbors of C1, C2, C4, and C6 are two carbon atoms and one hydrogen atom. Bond length changes related to C3 and C5 are smaller than those related to C1, C2, C4, and C6 when spinless-hole is injected. These smaller bond-length changes appear to be related to the decreasing of the magnetic moment of C3 and C5 atoms.

The total density of states (DOS) of ground-state and one spinless-hole injected Pc are shown in Fig.3. It is obvious that the ground-state is spin-degenerate. However, for one spinless-hole injected Pc, the DOS of the up and the down spins near the Fermi energy have undergone splitting, which indicates that the system is spin polarized. The obtained HOMO-LUMO (highest occupied molecular orbital-lowest unoccupied molecular orbital) gap for the ground-state Pc is 1.14 eV. For one spinless-hole injected Pc, the HOMO-LUMO gaps for the spin-up and the spin-down channels change to 1.06 and 1.02 eV, respectively. To investigate the mech-
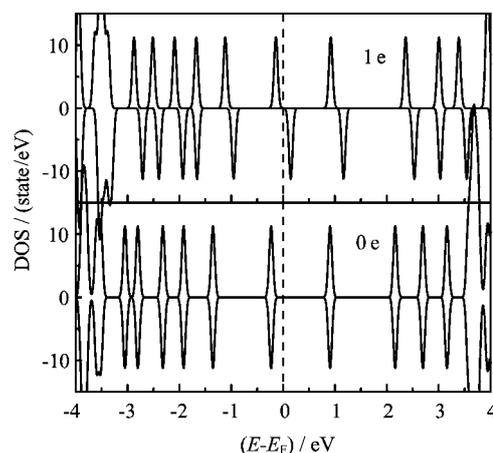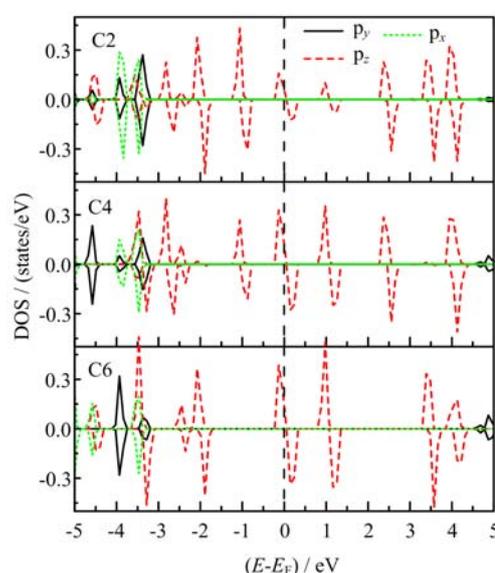

FIG. 4 The local DOS of several sample carbon atoms in one spinless-hole injected Pc.

anism of charge-induced spontaneous spin polarization in normal nonmagnetic Pc, we further give the local DOS of sample atoms C2, C4, and C6 in one spinless-hole injected Pc, which is shown in Fig.4. The HOMO and the LUMO consist only of atomic hybrid p-type orbitals. It is obvious that there are only p_z orbitals near the Fermi energy for all the sample atoms and the p_z orbitals are all spin-splitted due to the spinless-hole injection. So the injected hole firstly fills spin-splitted carbon p_z orbitals, which will make the system spin polarize. For the numerical value of the local DOS among the three sample carbon atoms, C6>C4>C2, so C6 will provide the largest magnetic moment contribution, C4 will be the next, and C2 will give the smallest magnetic moment contribution, which are consistent with the data in Fig.1. The magnetic moment contributions

of hydrogen atoms are near zero.

IV. CONCLUSION

Charge-induced spontaneous spin polarization in normal nonmagnetic Pc are studied by DFT calculations. It is shown that due to the existence of unpaired charge upon spinless-hole injection, there will be a net magnetic moment and the magnetic moment increases linearly with the increasing of the injected extra hole charge amount. Another consequence of spinless-hole injection is the different bond length changes of Pc. The injected spinless-hole will not equally fill all carbon orbitals but preferably fill the spin-splitted p_z orbitals near the Fermi energy, which makes the system spin polarize due to the different occupation of up and down spins.

V. ACKNOWLEDGMENTS

[1] A. Mishra and P. Bäuerle, Ange. Chem. Inter. Ed. **51**, 2020 (2012).

[2] V. Coropceanu, J. Cornil, D. A. da Silva Filho, Y. Olivier, R. Silbey, and J. L. Brédas, Chem. Rev. **107**, 926 (2007).

[3] Y. Lin, Y. Li, and X. Zhan, Chem. Soc. Rev. **41**, 4245 (2012).

[4] D. Voss, Nature **407**, 442 (2000).

[5] I. H. Campbell and D. L. Smith, Solid State Phys. **55**, 1 (2001).

[6] S. A. Wolf, D. D. Awschalom, R. A. Buhrman, J. M. Daughton, S. von Molnar, M. L. Roukes, A. Y. Chtchelkanova, and D. M. Treger, Science **294**, 1488 (2001).

[7] W. J. M. Naber, S. Faez, and W. G. van der Wie, J. Phys. D **40**, R205 (2007).

[8] V. A. Dediu, L. E. Hueso, I. Bergenti, and C. Taliani, Nature Mater. **8**, 707 (2009).

[9] Y. Y. Lin, D. Gundlach, S. Nelson, and T. Jackson, IEEE Electron Device Lett. **18**, 606 (1997).

[10] M. Shtein, J. Mapel, J. B. Benziger, and S. R. Forrest, Appl. Phys. Lett. **81**, 268 (2002).

[11] A. Ferretti, C. Baldacchini, A. Calzolari, R. D. Felice, A. Ruini, E. Molinari, and M. G. Betti, Phys. Rev. Lett. **99**, 046802 (2007).

[12] H. Jeong, D. Y. Jung, and H. W. Yeom, Phys. Rev. B **78**, 073305 (2008).

[13] K. Müller, A. Kara, T. K. Kim, R. Bertschinger, A. Scheybal, J. Osterwalder, and T. A. Jung, Phys. Rev. B **79**, 245421 (2009).

[14] K. Müller, A. P. Seitsonen, T. Brugger, J. Westover, T. Greber, T. Jung, and A. Kara, J. Phys. Chem. C **116**, 23465 (2012).

[15] B. Mahns, F. Roth, A. König, M. Grobosch, M. Knupfer, and T. Hahn, Phys. Rev. B **86**, 035209 (2012).

[16] H. Tanaka, M. Hirate, S. Watanabe, K. Kaneko, K. Marumoto, T. Takenobu, Y. Iwasa, and S. Kuroda, Phys. Rev. B **87**, 045309 (2013).

[17] M. Popinciuc, H. T. Jonkman, and B. J. van Wees, J. Appl. Phys. **100**, 093714 (2006).

[18] T. Shimada, H. Nogawa, T. Noguchi, Y. Furubayashi, Y. Yamamoto, Y. Hirose, T. Hitosugi, and T. Hasegawa, Jpn. J. Appl. Phys. **47**, 1184 (2008).

[19] Y. L. Chan, Y. J. Hung, C. H. Wang, Y. C. Lin, C. Y. Chiu, Y. L. Lai, H. T. Chang, C. H. Lee, Y. J. Hsu, and D. H. Wei, Phys. Rev. Lett. **104**, 177204 (2010).

[20] D. H. Wei, Y. L. Chan, Y. J. Hung, C. H. Wang, Y. C. Lin, Y. L. Lai, H. T. Chang, C. H. Lee, and Y. J. Hsu, Synth. Met. **161**, 581 (2011).

[21] J. Y. Hong, Y. M. Chang, C. H. Chuang, K. S. Li, Y. C. Jhang, H. W. Shiu, C. H. Chen, W. C. Chiang, and M. T. Lin, J. Phys. Chem. C **116**, 21157 (2012).

[22] S. Mooser, J. F. K. Cooper, K. K. Banger, J. Wunderlich, and H. Sirringhaus, Phys. Rve. B **85**, 235202 (2012).

[23] S. Alborghetti, J. M. D. Coey, and P. Stamenov, J. Appl. Phys. **112**, 124510 (2012).

[24] Y. Z. Wang, L. Cao, D. C. Qi, W. Chen, A. T. S. Wee, and X. Y. Gao, J. Appl. Phys. **112**, 033704 (2012) .

[25] K. Tarafder, B. Sanyal, and P. M. Oppeneer, Phys. Rev. B **82**, 060413(R) (2010).

[26] D. Hou, J. Qiu, S. Xie, and A. Saxena, New J. Phys. **15**, 073044 (2013).

[27] X. B. Yuan and J. F. Ren, J. Phys. Chem. C **117**, 16238 (2013).

[28] J. F. Ren, X. B. Yuan, and G. C. Hu, Chin. Phys. Lett. **31**, 048502 (2014).

[29] S. Han, H. Jiang, X. Li, and S. Xie, Org. Electron. **15**, 240 (2014).

[30] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993).

[31] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).