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姓 名	王佳	学号	2015931009	性 别	女	
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外语水平	CET-4	QQ 号	1103891789@qq.com	手机号码	15804318589	
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证书

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Charging-induced asymmetric spin distribution in an asymmetric (9,0) carbon nanotube†

Jia Wang,^{ab} Wim G. Roeterdink,^{ab} Wanrun Jiang,^{ab} Xing Dai,^{ab} Yang Gao,^{ab}
Bo Wang,^{ab} Yanyu Lei,^{ab} Zhigang Wang^{*ab} and Rui-Qin Zhang^{*cd}

Asymmetry in the electronic structure of low-dimensional carbon nanomaterials is important for designing molecular devices for functions such as directional transport and magnetic switching. In this paper, we use density functional theory to achieve an asymmetric spin distribution in a typical (9,0) carbon nanotube (CNT) by capping the CNT with a fullerene hemisphere at one end and saturating the dangling bonds with hydrogen atoms at the other end. The asymmetric structure facilitates obvious asymmetry in the spin distribution along the tube axis direction, with the maximum difference between the ends reaching $1.6 \text{ e } \text{Å}^{-1}$. More interestingly, the heterogeneity of the spin distribution can be controlled by charging the system. Increasing or decreasing the charge by $2e$ can reduce the maximum difference in the linear spin density along the tube axis to approximately $0.68 \text{ e } \text{Å}^{-1}$ without changing the proportion of the total electron distribution. Further analyses of the electron density difference and the density of states reveal the loss and gain of charge and the participation of atomic orbitals at both ends. Our study characterizes the asymmetric spin distribution in a typical asymmetric carbon system and its correlation with charge at the atomic level. The results provide a strategy for controlling the spin distribution for functional molecular devices through a simple charge adjustment.

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Introduction

Low-dimensional nanomaterials have attracted much attention due to their unique electronic properties that facilitate potential applications in mechanical, thermal, optical, and other fields.^{1–7} Compared with the geometric and electronic properties of symmetrical structures, asymmetric structures are more interesting in terms of target scattering,⁸ spin batteries,⁹ magnetic reconnection,¹⁰ and so on. Carbon nanomaterials are becoming more attractive, especially for use in pure carbon systems that are spin-polarized.^{11–14} The spin polarization effects of carbon-based nanomaterials have attracted much interest for their spin valve and spin injection in molecular devices,^{15–17} and even in biomedical drug delivery.¹⁸ However, few studies have looked at the design of molecular devices based on asymmetric spin distribution, even though this asymmetry is critical to targeted transport and magnetic switches.¹⁹

In low-dimensional carbon materials, spin polarization usually arises from localized electronic states at the edge of structures.^{11,19–24} For example, for the ground state of zigzag edge nanotubes, the spin polarization at an edge is ferromagnetic and antiferromagnetically coupled at the two zigzag edges.¹¹ Spin polarization is also closely related to the edge structure of nanomaterials. Graphene nanoribbons (GNRs) with zigzag edges (ZGNRs) have large spin polarization, while localized edge states are rarely seen for graphene ribbons with armchair edges (AGNRs).²⁰ In addition, because GNRs exhibit spin-polarized phenomena for at least three consecutive atoms at the zigzag edges,²¹ the number of edge atoms also has a large influence on spin polarization. Research on defects in nanomaterial structures shows that vacancies and doping also suppress the spin polarization of low-dimensional carbon materials to a certain extent.^{25,26} Theoretical simulations have also demonstrated that an external electric field might have the potential to influence the spin properties and that magnetic fields can change the spin ordering on zigzag edges.^{21,27} However, existing research focuses mainly on the properties of symmetrical neutral systems.

Density functional theory (DFT)^{28–30} is widely accepted as a suitable tool for understanding the characteristics of the geometric and electronic structures of carbon material systems.^{3,11,19,21,31–35} DFT methods have been used to deal with sp^2 hybridized electronic structures in low-dimensional carbon systems with a variety of

^a Institute of Atomic and Molecular Physics, Jilin University, Changchun 130012, China. E-mail: wangzg@jl.u.edu.cn

^b Jilin Provincial Key Laboratory of Applied Atomic and Molecular Spectroscopy (Jilin University), Changchun, 130012, China

^c Department of Physics and Materials Science and Centre for Functional Photonics (CFP), City University of Hong Kong, Hong Kong SAR, China. E-mail: aprqz@cityu.edu.hk

^d Beijing Computational Science Research Center, Beijing 100084, China

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PAPER

Chirality dependent spin polarization of carbon nanotubes

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Jia Wang^{1,2}, Wanrun Jiang^{1,2}, Bo Wang^{1,2}, Yang Gao^{1,2}, Zhigang Wang^{1,2} and Rui-Qin Zhang^{3,4}¹ Institute of Atomic and Molecular Physics, Jilin University, Changchun, 130012, People's Republic of China² Jilin Provincial Key Laboratory of Applied Atomic and Molecular Spectroscopy (Jilin University), Changchun, 130012, People's Republic of China³ Department of Physics and Materials Science and Centre for Functional Photonics (CFP), City University of Hong Kong, Hong Kong SAR, People's Republic of China⁴ Beijing Computational Science Research Center, Beijing 100084, People's Republic of China

E-mail: wangzg@jlu.edu.cn and aprqz@cityu.edu.hk

Keywords: spin polarization, chirality, carbon nanotubes, density functional theory

Supplementary material for this article is available online

Abstract

The spin polarization of carbon nanotubes (CNTs) offers a tunable building block for spintronic devices and is also crucial for realizing carbon-based electronics. However, the effect of chiral CNTs is still unclear. In this paper, we use the density functional theory (DFT) method to investigate the spin polarization of a series of typical finite-length chiral CNTs (9, *m*). The results show that the spin density of chiral CNTs (9, *m*) decreases gradually with the increase in *m* and vanishes altogether when *m* is larger than or equal to 6. The armchair edge units on both ends of the (9, *m*) CNTs exhibit a clear inhibition of spin polarization, allowing control of the spin density of (9, *m*) CNTs by adjusting the number of armchair edge units on the tube end. Furthermore, analysis of the orbitals shows that the spin of the ground state for (9, *m*) CNTs mainly comes from the contributions of the frontier molecular orbitals (MOs), and the energy gap decreases gradually with the spin density for chiral CNTs. Our work further develops the study of the spin polarization of CNTs and provides a strategy for controlling the spin polarization of functional molecular devices through chiral vector adjustment.

1. Introduction

Low-dimensional carbon materials show great potential in realizing spin polarized injectors [1, 2], spin transport [3, 4], spin valves [5, 6], and similar molecular devices due to their capabilities to present of spin polarized electronic structures. Studies show that for the ground state of finite-length zigzag edge carbon nanotubes (CNTs), the spin polarization is ferromagnetically coupled among the atoms at one end and antiferromagnetically coupled between the two zigzag edges [7–9], similar to the coupling seen in some graphene fragments [10, 11]. Further research on defects in low-dimensional carbon materials shows that vacancies and doping at the zigzag edges suppresses their spin polarization [11]. It is clear that the magnetism involved in these carbon-based materials arises mainly from the spin polarizations of local structural defects [12–18] rather than perfect structures. In particular, the local defect structure dependence of the spin polarization can be seen clearly in the different characteristics of CNTs with pure zigzag or pure armchair edges. The former demonstrates considerable spin polarization, as shown in both theoretical and experimental studies [7, 19–23], while the latter shows none [10]. A recent study of graphene nanoflakes (GNFs) shows that eliminating the armchairs region between the zigzag edges significantly improves their spin-polarized properties, such as magnetic coupling [24].

As both zigzag and armchair edges are present in chiral CNTs (*n*, *m*) (*n* ≠ *m* ≠ 0) at each end, side by side [25, 26], their spin polarization can be very complicated. It is hoped that it can be controlled by tuning the values of the chiral vectors *m* and/or *n*. The study of such tunable spin polarization will be significant in molecular device applications, but unfortunately no work has yet been done on this. In related work, a study of graphene nanoribbons (GNRs) has identified spin-polarized phenomena for at least three consecutive zigzag units at the

FULL PAPER

The self-consistent charge density functional tight-binding theory study of carbon adatoms using tuned Hubbard U parametersJia Wang^{1,2†} | Xing Dai^{1,2†} | Wanrun Jiang^{1,2} | Tianrong Yu^{1,2} | Zhigang Wang^{1,2}¹Institute of Atomic and Molecular Physics, Jilin University, Changchun 130012, China²Jilin Provincial Key Laboratory of Applied Atomic and Molecular Spectroscopy (Jilin University), Changchun 130012, China

Correspondence

Zhigang Wang, Institute of Atomic and Molecular Physics, Jilin University, Changchun 130012, China.
Email: wangzg@jlu.edu.cn or wangzg1978@hotmail.com

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Abstract

The self-consistent charge density functional tight-binding (DFTB) theory is a useful tool for realizing the electronic structures of large molecular complex systems. In this study, the electronic structure of C_{61} formed by fullerene C_{60} with a carbon adatom is analyzed, using the fully localized limit and pseudo self-interaction correction methods of DFTB to adjust the Hubbard U parameter (DFTB + U). The results show that both the methods used to adjust U can significantly reduce the molecular orbital energy of occupied states localized on the defect carbon atom and improve the gap between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of C_{61} . This work will provide a methodological reference point for future DFTB calculations of the electronic structures of carbon materials.

KEYWORDS

density functional tight-binding, Hubbard U parameter, p electron, spin polarization

1 | INTRODUCTION

Carbon adatoms are one of the sources of intrinsic magnetism in low-dimensional carbon systems^[1,2] such as graphene, carbon nanotubes (CNTs), and fullerenes. This kind of defect is usually a carbon atom absorbed at a C–C bond between two hexagons (bridge-sites) in a carbon system. Here, we explain the electron behavior of this kind of absorbed atom using a simple theoretical model, as shown in Figure 1. In general, in this type of carbon system, every carbon atom has four valence electrons, three sp^2 electrons and one electron in p_z orbitals.^[3,4] However, two sp^2 electrons of the adatom form two sigma bonds with two sp^2 electrons from adjacent carbon atoms, leaving the sp^2 electron in the Y -direction (Figure 1A). Meanwhile, the remaining electron in p_z orbitals of the adatom cannot bond with any electron from the other atoms (Figure 1B). Therefore, there are two electrons that are spin-polarized for the adatom.


Experimental studies have shown that these adsorbed defects have magnetic moments which arise from the spin polarization of ad-

atomic electrons.^[5] Several previous studies using conventional density functional theory (DFT) have also confirmed this theoretical model.^[6–9]

Compared to first-principles, in particular DFT, the self-consistent charge density functional tight-binding method (SCC-DFTB, hereafter abbreviated as DFTB) provides a new extension and analysis platform for quantum calculations^[10] and is aimed at giving a good approximation for DFT results. In DFTB, only the two-center integral Hamiltonian and overlap matrix elements are included, with the three-center integral neglected and a short-range repulsive potential used.^[11] Thus, the DFTB method has attracted much attention because of its higher computational efficiency^[12] in dealing with pure carbon systems, the interactions between carbon systems with other molecules as well as the dynamics of biological systems and other large systems^[13–15] and gets relatively reliable results. In addition, parametrizations of the DFTB method has also been widely studied recently.^[16–18] For both solid^[19–22] and molecular systems,^[23,24] the original form (i.e., non-SCC form)^[25] and the SCC form^[26] of the DFTB method all show wide applications. However, we must be especially careful in investigating some particular areas (mainly d and f regions) of the periodic table by DFT and its related methods, owing to false DFT self-interactions in

[†]These authors contributed equally to this study.

Structural Asymmetry-Facilitated Tunability of Spin Distribution in the (10, 0) Carbon Nanotube Induced by Charging

JIA WANG,^{1,2} YANG GAO,^{1,2} ZHIYUAN ZHANG,^{1,2} DEXUAN XU,^{1,2}
ZHIGANG WANG ^{1,2,5} and RUI-QIN ZHANG^{3,4,6}

1.—Institute of Atomic and Molecular Physics, Jilin University, Changchun 130012, China. 2.—Jilin Provincial Key Laboratory of Applied Atomic and Molecular Spectroscopy, Jilin University, Changchun 130012, China. 3.—Department of Physics and Materials Science and Centre for Functional Photonics (CFP), City University of Hong Kong, Kowloon Tong, Hong Kong SAR, China. 4.—Beijing Computational Science Research Center, Beijing 100084, China. 5.—e-mail: wangzg@jlu.edu.cn. 6.—e-mail: aprqz@cityu.edu.hk

Constructing the asymmetric electronic structure of low-dimensional carbon nanomaterials is significant for application of molecular devices, such as magnetic switches. In this work, we use density functional theory to investigate the asymmetric spin distribution in a typical (10, 0) carbon nanotube by capping one end with a fullerene hemisphere and saturating the dangling bonds with hydrogen atoms at the other end. Calculated results indicate that this geometry obviously modified the distribution of spin density along the tube axis, and the electrons present were antiferromagnetically coupled at both ends. Specifically, the change in magnetic order at the end of the cap can be changed with either the increase or decrease of the charge. In addition, the analysis of electron density difference shows that charge induces gain or loss of electrons not only at the open end, but also at the cap end. These findings provide a strategy for controlling spin distribution for nanoscale functional molecular devices through a simple charge adjustment.

Key words: Carbon nanotube, spin polarization, electronic structure, density functional theory

INTRODUCTION

Carbon nanotubes (CNTs) have been widely applied in many fields such as boat hulls, thin-film, rechargeable batteries and sporting goods, etc.^{1–3} In addition, they have also drawn attention for energy storage,⁴ water purification⁵ and toxin detection.⁶ The electronic structure of low-dimensional asymmetric carbon nanomaterials is important for designing molecular devices such as biomedical imaging and magnetic switching.^{7,8} Furthermore, the previous research of (9, 0) CNTs capped with a C₃₀ hemisphere displays asymmetrical electronic properties, and increasing or decreasing charge can adjust its spin distribution.⁹ Cap-(9, 0) and Cap-(10, 0) are the only two zigzag CNTs that can be capped,

and their different diameters indicate different confinements. However, the impact of structural difference on electronic populations is still not clear.

For low dimensional carbon nanomaterials, the magnetism is mainly derived from the spin polarizations of local structural defects,^{10,11} especially, it is well known from localized electronic states of structure with zigzag edges of graphene and CNTs.^{12–15} Studies show that vacancies and doping can significantly modify spin polarization, and, consequently, the electronic and magnetic properties of SWCNT are dependent on defects and doped impurities.^{14,16–18} Previous theoretical simulations have demonstrated that an external electric field might have an effect on spin properties such as magnetic fields that can change the spin ordering at zigzag edges.^{19,20}

Density functional theory (DFT) is a quantum mechanics method for studying the electronic

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All-boron Fullerene B₄₀: A Superatomic Structure

Jia Wang^{1,2†}, Tianrong Yu^{1,2†}, Yang Gao^{1,2} and Zhigang Wang^{1,2*}

ABSTRACT Herein, by means of first-principles calculations, we reveal that B₄₀ presents superatomic properties. It not only has superatomic 1S, 1P, 1D and 1F orbitals, but also has superatomic orbitals 2S, 2P, 2D and 2F. The superatomic 2F orbital of B₄₀ is partially occupied, thus adding six electrons to the cluster leads to a superatomic structure of fully occupied shells. The computed nucleus-independent chemical shift values suggest that B₄₀⁶⁻ is of higher electron delocalization than B₄₀ itself. Our work opens up a new perspective for the superatomic physics in the boron fullerene family.

Keywords: Boron fullerene, Superatom, Electronic structure, First-principles

INTRODUCTION

The all-boron fullerene B₄₀, discovered in 2014, has greatly enriched the chemistry of boron and may lead to the development of new boron-based nanomaterials [1]. Subsequently, the stabilities and electronic properties of endohedral metal complexes of B₄₀ have also been investigated [2-4]. Among the clusters with various sizes, those deemed "superatoms" exhibit enhanced stabilities due to the electronic shell closing [5]. Many superatomic structures, such as C₆₀ [6], Al₁₃ [7], Na₄₀ [8] and Au₂₀ [9], have been experimentally confirmed. Recently, the Au₃₂ gold fullerene was revealed to have 1S²1P⁶1D¹⁰1F¹⁴ electronic configuration, thus making it a superatom [10, 11]. Similarly, as a hollow cage structure, is B₄₀ fullerene also a superatom? Answering this question is crucial for us to understand the stabilities of B₄₀ and its derivatives, and explore their potential applications.

In this work, by means of density functional theory (DFT) computations [12], we carefully analyzed the nature of electronic structure of the all-boron fullerene B₄₀. Our calculations revealed that the neutral B₄₀ fullerene is a superatom with partially occupied 2F shell. However, by adding six electrons or removing eight electrons, a superatom can be formed with fully occupied shells. In addition, B₄₀⁶⁻ and B₄₀⁸⁺ with fully occupied shells are highly aromatic as indicated by the negative nucleus-independent chemical shift (NICS)

values at the cage center.

THEORETICAL SECTION

The geometric structure of B₄₀ was fully optimized using generalized gradient approximation (GGA) functional PBE [13] and hybrid functionals PBE0 [14], B3LYP [15, 16] and HSE06 [17, 18] with 6-31G* basis sets [19], and the relative energies between different electronic states was listed in Table S1 in Supporting Information (SI). The charged species of B₄₀, namely, B₄₀⁶⁻ and B₄₀⁸⁺, were also optimized at PBE0/6-31G* level. Frequency analyses were performed at the same level of theory to characterize the nature of the stationary points. Both B₄₀ and B₄₀⁶⁻ are true local minima, but B₄₀⁸⁺ with fully occupied shell is a high order saddle point. Following the imaginary modes of B₄₀⁸⁺ led to the true local minimum without full-filled shell. The optimized geometries from different functionals are rather similar, and we only discussed the computational results from PBE0 because it has been tested extensively in previous works and found to be suitable for boron clusters.[1, 20-22] To investigate the electron delocalization or aromaticity of B₄₀ and its charged species, we calculated NICS (in ppm) [23, 24] at the cage centers of the optimized geometries of the empty cage molecules using the gauge-independent atomic orbital (GIAO) method [25]. The verification of B₄₀ using PBE0/6-311+G* level is shown in Table S2 in SI. All computations are carried out using the Gaussian09 package [26].

RESULTS

Our calculations showed that the ground state of B₄₀ fullerene (D_{2d}) is non-spin-polarized singlet, with the low and high energy molecular orbitals (MOs) displayed in Figures 1 and 2, respectively. Among the low-energy MOs, a double-occupied MO 7a₁ (marked by black) resembles an s-like atomic orbital, thus we called it the 1S superatomic orbital (that is, molecular orbital) for B₄₀, and the specific orbital composition analysis are described in the following. This 1S orbital is followed by three p-like atomic orbitals, namely, the 6b₂ and 11e MOs (denoted by red), which are actually the 1P superatomic orbitals of B₄₀. Then, there are five d-like orbitals, namely, 5b₁, 12e, 8a₁ and 7b₂ (marked by blue), which are the 1D superatomic orbitals for B₄₀

¹Institute of Atomic and Molecular Physics, Jilin University, Changchun 130012, China

²Jilin Provincial Key Laboratory of Applied Atomic and Molecular Spectroscopy (Jilin University), Changchun 130012, China

[†]These authors contributed equally to this paper

*Corresponding author (email: wangz1978@hotmail.com or wangzg@jlu.edu.cn)