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Ph. D. Dissertation

탄소 나노튜브의 물리적 특성에 대한 이론 연구

Theoretical study on physical properties of carbon nanotubes

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A thesis submitted to the faculty of KAIST in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Physics . The study was conducted in accordance with Code of Research Ethics[1].

2002. 12. 5.

Approved by

Professor Chang, Kee Joo

[Advisor]

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[1]Declaration of Ethical Conduct in Research: I, as a graduate student of KAIST, hereby declare that I have not committed any acts that may damage the credibility of my research. These include, but are not limited to: falsification, thesis written by someone else, distortion of research findings or plagiarism. I affirm that my thesis contains honest conclusions based on my own careful research under the guidance of my thesis advisor.

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ABSTRACT

For the last decade, carbon nanotubes have been emerging as one of ideal materials for the building block of the forthcoming nanotechnology, due to their unique electrical and mechanical properties. Depending on detailed wrapping-up methods, their electronic properties show a wide spectrum from metals to large-gap semiconductors with band gaps of 1eV. In this thsis, we study various physical properties of carbon nanotubes, including electrical properties and their controlling methods, magnetic properties, and transport characteristics, based on the first-principles density-functional theory and the tight-binding model.

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Chapter 1. Introduction

In 1991, Dr. Iijima at the NEC in Tsukuba published his celebrated paper in Nature with the title of "Helical Microtubules of Graphitic Carbon" [**?**]. It has brought great impact to various fields of physics, chemistry, and material science [**?**, **?**]. Because of their intrinsic nanometric size, the "microtubules" are renamed as "carbon nanotubes" and can be regarded as ideal materials for realizing the forthcoming nanotechnology. Depending on the "helicity', a wide spectrum of electronic structure from metal, small-gap (a few meV) to large-gap ($\sim$ 0.5 eV) semiconductors is expected. People thinks that they can make nano-sized electronic devices like field-effect transistors, diodes, and their integrated circuits with carbon nanotubes. Most of physical properties of carbon nanotubes originates from those of "graphite": anisotropic electrical properties, strong mechanical strength, and flexibility.

Chapter 2. Electrical properties

2.1 Band gap control by radial deformation

In this work we report on a band gap modification by radial deformation in carbon nanotubes, based on theoretical calculations of the electronic structures. Such band gap modification has important implication in nanodevices such as quantum dots and metal-insulator junctions. In fact, it was proposed that nanotube-based quantum dots or metal-insulator junctions can be made by introducing topological defects such as pentagon-heptagon pairs. Based on composite $B_xC_yN_z$ nanotubes, the possibility of nanodevices by doping or composition control has also been suggested. In view of this, our band gap modification only depends on mechanical radial deformation and is quite easier to achieve.

2.2 Band gap control by transverse electric fields

Here we investigate the effect of various environments such as flattening deformations, transverse electric fields, and electrodes on the electronic and transport properties of single-wall carbon nanotubes through first-principles pseudopotential and tight-binding calculations. Using a perturbative approach, we analyze the periodicity of external potentials along the circumferential direction, and find that selection rules exist in subband mixings. For the (17,0) and (40,0) tubes under electric fields perpendicular to the tube axis, both the tubes undergo a semiconductor-metal transition, while the band gap of the (40,0) nanotube with a larger diameter decreases more rapidly. On the other hand, in the metallic (18,0) tube, a gap is generated near the Fermi level, resulting in zero transmission.

Chapter 3. Magnetism

3.1 Magnetic carbon and defective C_{60}

Following the recent discovery of ferromagnetism at room temperature in an all-carbon system consisting of polymerized C_{60} [**?**], there has been increased interest in magnetism in metal-free systems. Even though this finding is a significant step in the long-standing search for novel high-temperature magnets [**?**], the origin of this magnetism is still unclear, and possibly linked to defects.

We first think of cage opening process in C_{60} by breaking relatively weak single bonds. Breaking the single bonds introduce the well-known Stone-Wales (SW) transformation [**?**]. We find a set of metastable open cage structure for forming a (5,5) capsule by introducing successive SW-type bond rotations, as shown in Fig. **??**. From perfect C_{60}, buckminsterfullerene (BF), five SW bond rotations complete transformation to the (5,5) capsule, CAP(5,5). Naming after the number of the SW transformation, we call them as SW-I, SW-II, and SW-III. In these structures, the coordination of all carbon atoms is 2 or 3. We exclude the SW-IV because of one coordination of a carbon atom that are very unstable. In Fig. **??**, we highlight the undercoordinated carbon atoms. In the cases of SW-I and SW-II, two highlighted atoms are in armchair arrangement, and the other two are in zigzag arrangement. The zigzag arrangements in SW-I and SW-II are little different from each other. In SW-I, two zigzag atoms are connected in an armchair bridge, while in SW-II they are connected as like the normal zigzag edge.

Energy stabilities are summarized at Table **??**. Except SW-I and SW-II where zigzag-type atoms appear, non-magnetic configuration is favorable even in the presence of undercoordinated atoms. The dangling bond in armchair-type atoms is passivated by forming a double bond between them, of which length is about 1.239 Å. Due to the slight difference of arrangement of zigzag-type atoms, SW-I favors a paramagnetic (Para) configuration in amount of 36 meV, while SW-II does a ferromagnetic (Ferro) configuration in gain of 10 meV. The net magnetic moment corresponds to two unpaired electrons.

In conclusion, we find metalstable C_{60} isomers with open cage structure, which show magnetic instability including favorable ferromagnetic spin configurations. This could be a possible mechanism for recently reported room temperature ferromagnetism in polymerized C_{60} solids.

3.2 C/BN heterostructured nanotubes

In conclusion, we used local spin density functional calculations to study the occurrence of magnetism in quasi one-dimensional heterostructured C/BN nanotubes free of metallic impurities. At the zigzag boundary connecting carbon and boron nitride segments of tubes, we found atomic-like states that acquire magnetization when partly filled. Whereas individual C/BN heterojunctions can be used to spin polarize electrons during transport, periodic arrangements of heterojunctions in doped systems can lead to the formation of a one-dimensional itinerant ferromagnetic state.

Table 3.1: Energy stability E (eV) per molecule of all meta-stable isomer states of C_{60} opening process for forming the (5,5) cap. In the SW-I and SW-II, both ferromagnetic (Ferro) and paramagnetic (Para) spin configurations are obtained, whereas only non-magnetic configuration is obtained in the BF, SW-III, and CAP(5,5). M is total magnetization n_{up}-n_{down} in unit of μ_B, where $n_{\mathrm{up(down)}}$ is the number of up (down) spins.

	BF	SW-I		SW-II		SW-III	CAP
		Para	Ferro	Para	Ferro		
E (eV)	0	7.796	7.832	10.418	10.408	11.5	13.2
M (μ_B)	0	0	1.94	0	2.06	0	0

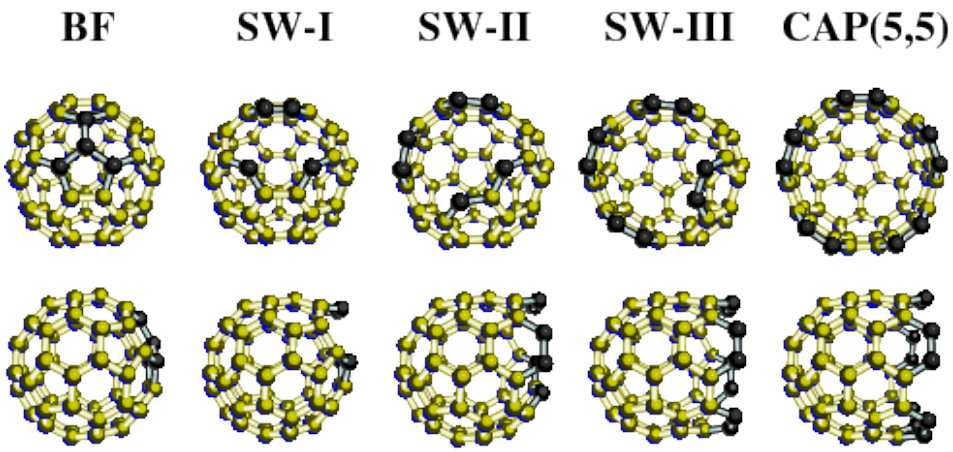

Figure 3.1: Ball-and-stick models of meta-stable isomers in cage opening process from a C_{60} buckminsterfullerene to a (5,5) capsule. We name them BF and CAP(5,5). Depending on the number of the Stone-Wales (SW) transformation, we call the intermediate isomers with SW-I, SW-II, and SW-III. Highlighted atoms are undercoordinated except BF.

Chapter 4. Conclusion

We discuss potentiality of metal-free ferromagnetism in pure carbon systems and their hybrids. We present possible C_{60} isomers for occurrence of magnetic instability. Partly open cages with zigzag edges may play a crucial role in the pure carbon magnets. We also propose occurrence of one-dimensional magnetism in carbon and BN heterostructured nanotubes. Due to the doubly degenerated states at the borders between carbon and BN nanotube segments, we find that Hund's rule-type occupation occurs when we dope the systems. When the adjacent border states overlap with each other, our calculations show that magnetic ordering is favorable.

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Summary

Theoretical study on physical properties of carbon nanotubes

지난 10여 년간 탄소 나노튜브는 자체의 독특한 전기적, 기계적 성질로 인하여 다가오는 나노기술 분야의 이상적인 기초물질중의 하나로 떠오르고 있다. 흑연을 감는 세세한 방법에 따라 전기적 특성이 금속성에서 1eV의 띠간격을 가지는 반도체 특성까지 다양한 분포로 존재한다. 본 학위논문에서는 탄소 나노튜브의 여러 물리적 성질에 대해 고찰하는데, 기본적으로 제일원리 밀도함수 이론과 밀접결합근사 모형을 사용하여 전기적 특성과 그 제어 방법, 자기적 특성, 그리고 수송특성 등을 다루고자 한다.

감 사 의 글

이 논문을 완성하기까지 주위의 모든 분들로부터 수많은 도움을 받았습니다.

끝으로 오늘의 제가 있을 수 있도록 사랑으로 키워 주신 어머니와 또한 가족들에게 감사드립니다. 저의 이 작은 결실이 그분들께 조금이나마 보답이 되기를 바랍니다.

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연 구 업 적

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