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FIRST-PRINCIPLES INVESTIGATION OF CHIRALITY-DEPENDENT ELECTRONIC PROPERTIES IN CARBON NANOTUBES

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ABSTRACT

The electronic properties of single-walled carbon nanotubes (SWCNTs) are strongly influenced by their chirality, which plays a crucial role in determining their suitability for applications in nanoelectronics, energy storage, and other advanced technologies. In this study, we present an ab initio modeling framework for predicting the Fermi energy distribution in SWCNTs as a function of their chiral indices. Using first-principles calculations based on density functional theory (DFT), we systematically investigate the electronic structures of SWCNTs with chiral vectors (n, m), where n = 4, 5, 6 and m = 0. Our results indicate that these specific chiralities yield metallic behavior, as evidenced by the absence of a band gap. This computational approach provides fundamental insights into the chirality-dependent electronic behavior of carbon nanotubes, thereby supporting the rational design of carbon-based nanomaterials tailored for specific electronic applications.

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1. Introduction

Single-walled carbon nanotubes (SWCNTs) have attracted significant interest due to their exceptional electronic properties, which are highly sensitive to their chirality—the geometric arrangement of carbon atoms defined by chiral indices (n,m) [1,2]. This chirality dependence directly impacts their classification as metallic or semiconducting; with armchair nanotubes consistently exhibiting metallic behavior, while zigzag and chiral variants display either semiconducting or metallic properties depending on specific chiral values [3,4]. These characteristics make SWCNTs highly suitable for integration into nanoelectronic, energy storage, and sensing devices [5].

Traditional *ab initio* approaches, such as density functional theory (DFT), have been widely used to explore the electronic structure of SWCNTs with various chiralities [6,7].

While DFT provides accurate insight into band structure and Fermi energy distributions, it is computationally intensive, especially when extended to a large and diverse set of nanotube configurations [8]. To address this limitation, our study introduces a hybrid modeling framework that integrates DFT-based calculations with machine learning techniques to predict the Fermi energy distribution in SWCNTs as a function of chirality. Specifically, we focus on nanotubes with chiral vectors (n,0) for n=4, 5, 6, representing a class of zigzag SWCNTs known for their metallic behavior under certain conditions.

The proposed approach not only reduces the computational cost associated with large-scale quantum mechanical simulations but also captures underlying trends in the electronic behavior of carbon nanotubes with varying chiralities. By accurately modeling the Fermi energy across different structural configurations, our method provides a scalable pathway for the rational design of SWCNT-based nanomaterials tailored for specific technological applications in electronics, optoelectronics, and energy systems [9,10].

2. Computational Methods

This study combines ab-initio modeling to predict the Total Density of States (TDOS) distribution in single-walled carbon nanotubes (SWCNTs) with varying chirality, specifically from (4,0) to (6,0). The simulations were performed using Density Functional Theory (DFT), implemented in the Atomistic Tool Kit - Virtual Nano Laboratory (ATK-VNL) code. The Local Density Approximation (LDA) within DFT was employed for the calculations.

The Carbon-Carbon bond length was set to 1.42 Å. For each CNT system, chiral configurations ranging from (4,0) to (6,0) were generated to study how the band gap varies with the chirality of the nanotubes. The electron-ion and electron-electron interactions were treated using FHI ionic pseudopotentials and predefined Perdew-Zunger (PZ) functionals.

For the single-walled chiral CNTs with indices (n=4-6; m=0), Monkhorst-Pack (MP) grids of 1×1×5 k-sampling were used. All atomic positions were geometrically optimized during the calculations. Carbon atoms were considered with a valence configuration of C + [He] $2s^2$ $2p^2$, and a kinetic energy cutoff of 50 Ha was employed to ensure full convergence of the total energy calculations. The convergence criteria for the geometry optimization of the studied nanostructures, which contain 16, 20, and 24 atoms, were set to force tolerances of no higher than 0.05 eV/Å and stress tolerances of 0.1 GPa.

1. Results and Discussion

3.1. Electronic properties of CNT

Several studies have been devoted to investigating the electronic properties of single-walled chiral carbon nanotubes (SWCNTs). In Ref. [7], the authors reported first-principles calculations of the electronic properties of SWCNTs with chiralities (6,0) and (8,0) using Density Functional Theory (DFT) implemented in the Vienna Ab Initio Simulation Package (VASP). Matsuda et al. [8] conducted ab initio quantum mechanical predictions of electronic band structures for SWCNTs with zigzag structures using the B3LYP functional within DFT. Barone et al. [9] also examined optical properties of SWCNTs with DFT-LDA, DFT-PBA, and DFT-B3LYP simulations, noting that LDA and GGA functionals generally yielded lower values (~0.4 eV) compared to B3LYP. The experimental analysis of the electronic properties of SWCNTs from scanning tunneling microscopy (STM) measurements shows that the zigzag structure with (9,0) chirality exhibits a band gap of 0.080 ± 0.005 eV [10], which agrees with our results.

In this section, we calculated the electronic band structures, total density of states (TDOS), and partial density of states (PDOS) for SWCNTs with various diameters, specifically for chiralities (n=4, 5, 6; m=0). It is well-known that many physical and chemical properties of SWCNTs are highly dependent on their chirality, and these properties do not exhibit a simple monotonic trend. The band gap of SWCNTs can range from 0 eV to approximately 2 eV, and these nanotubes can either exhibit semiconducting or metallic behavior. CNTs are not strictly semi-metallic because the degeneracy point is slightly shifted from the K symmetry point in the Brillouin zone (BZ). This results in the π-bonding and π*-anti-bonding energy bands meeting at the Fermi level, causing the band gap to approach zero eV. This behavior arises due to the curvature of the nanotube surface, which induces hybridization between the σ*- and π*-anti-bonding energy bands, modifying the electron band dispersions. Based on the computed electronic band structures, we estimated the band gap for all studied 1D SWCNT nanosystems with chiralities ranging from (4,0) to (6,0). Our first-principles calculations indicate that the SWCNTs containing 16, 20, and 24 atoms exhibit metallic characteristics with a band gap of 0 eV, in agreement with recent computational studies.

Table 1. First principles results for single walled CNT systems with different chirality

System	Chirality	Diameter, Å		Band gap, eV	
		This work	Ref.	This work	Ref.
C_{16}	(4,0)	3.13	-	0	-
C_{20}	(5,0)	3.98	-	0	0 **[8]**
C_{24}	(6,0)	4.70	4.76 [7] 4.89 [8]	0	0 [7]

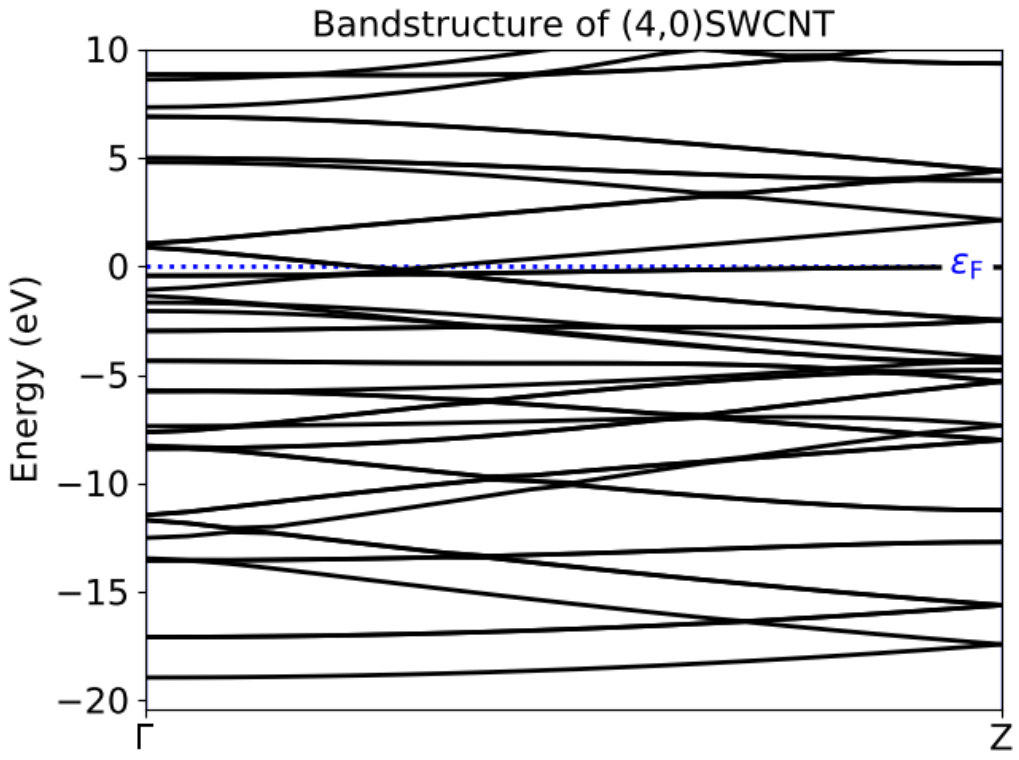

Fig. 1 First-principles calculated band structure for SWCNT with chirality (4,0)

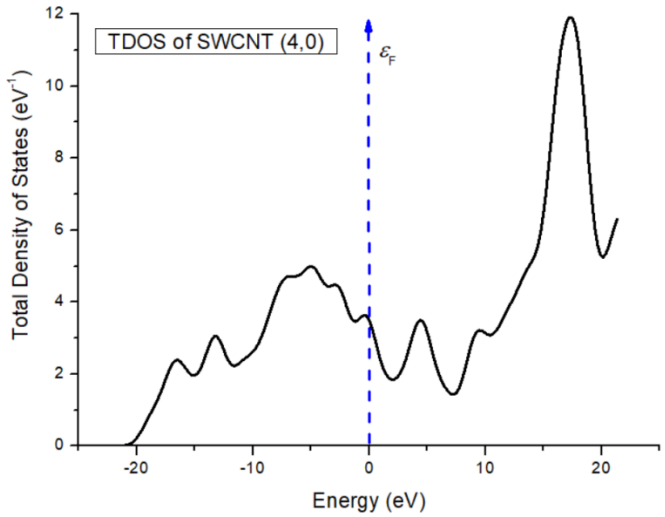

Fig. 2 First-principles calculated total density of states for SWCNT with chirality (4,0)

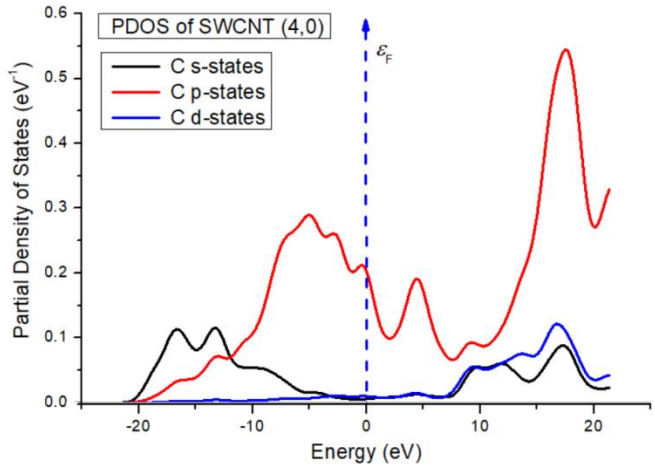

Fig. 3 First-principles calculated partial density of states of carbon in SWCNT with chirality (4,0)

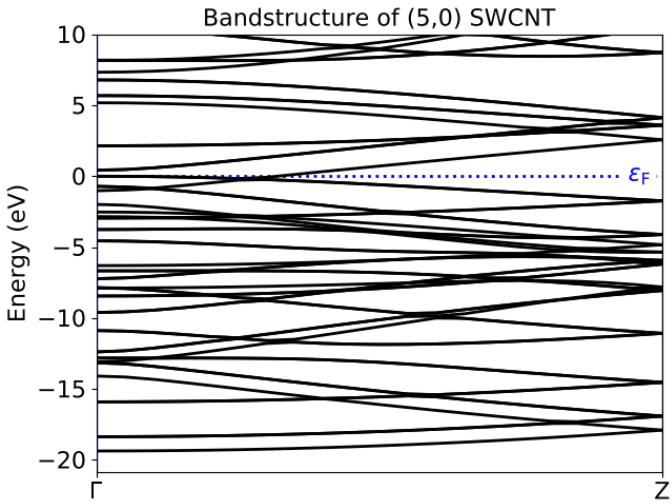

Fig. 4 First-principles calculated band structure for SWCNT with chirality (5,0)

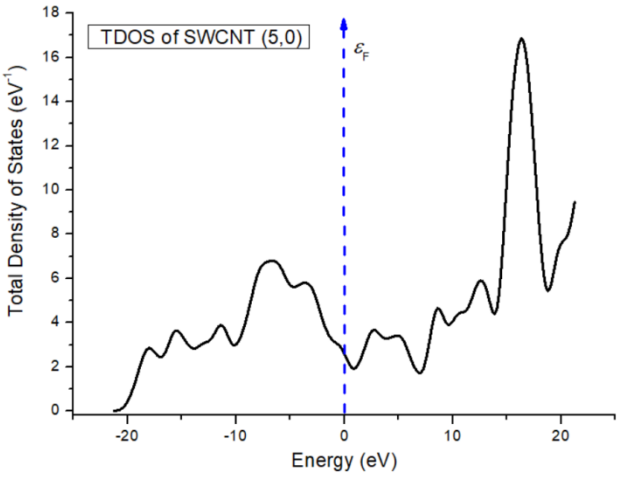

Fig. 5 First-principles calculated total density of states of SWCNT with chirality (5,0)

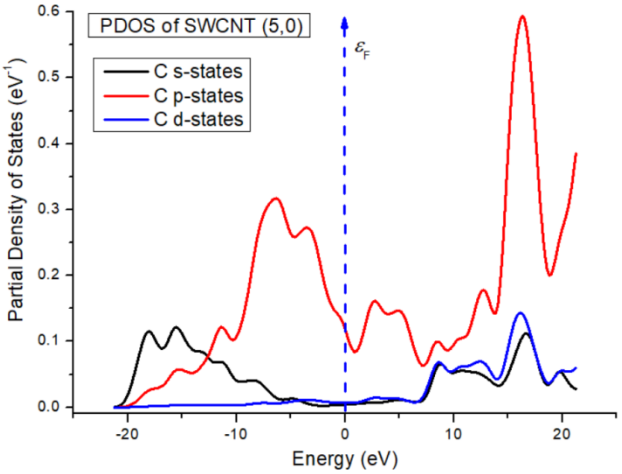

Fig. 6 First-principles calculated partial density of states of carbon in SWCNT with chirality (5,0)

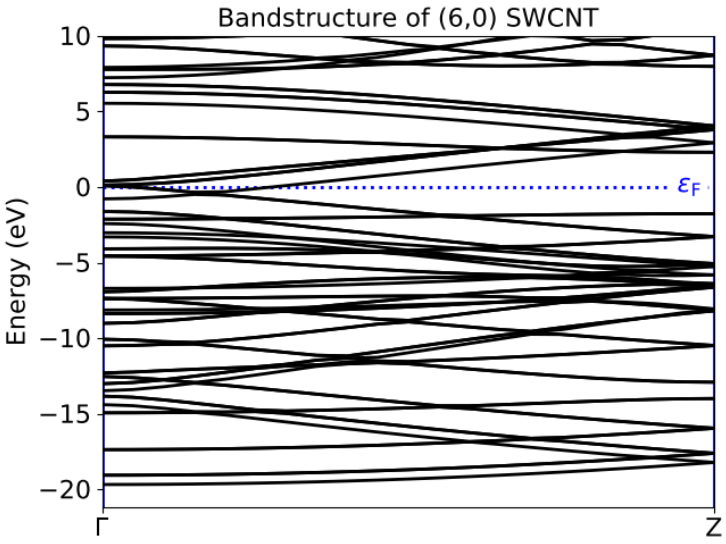

Fig. 7 First-principles calculated band structure for SWCNT with chirality (6,0)

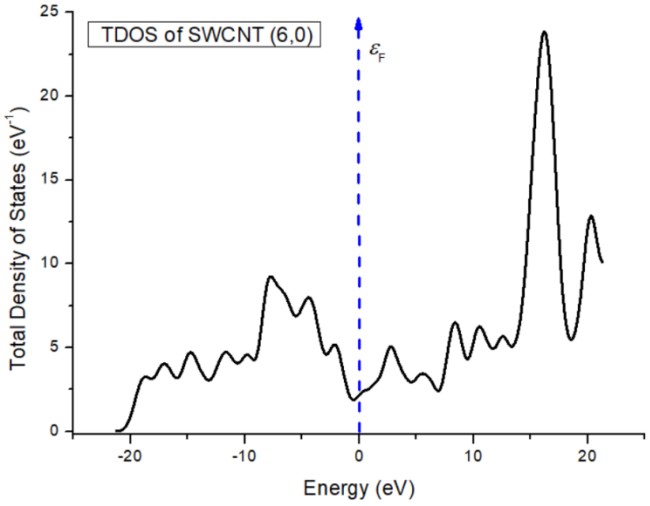

Fig. 8 First-principles calculated total density of states of SWCNT with chirality (6,0)

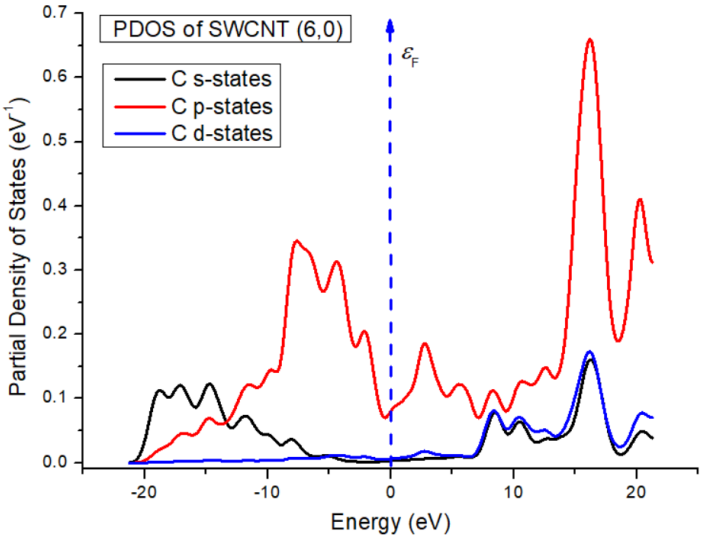

Fig. 9 First-principles calculated partial density of states of carbon in SWCNT with chirality (6,0)

C_{20} has a band gap of 0 eV in the study by [8] and C_{24} was reported with a range of 4.76 eV [7] and 4.89 eV [8]. From the first-principles results, we determined that all studied systems are direct band gap materials, where both the top of the valence band and the bottom of the conduction band are located at the center of the Brillouin zone (Γ-Γ transition). These findings are summarized in Table 1. The calculated electronic band structures, TDOS, and PDOS for SWCNT nanosystems with different chiralities (n=4-6; m=0) are shown in Figs. 2-9. In these figures, the Fermi energy level is set to zero electron volts, as indicated by the dotted lines. We observed that certain energy levels in the computed electronic band structures cross the Fermi energy, indicating that the SWCNT systems with chiralities (n=4, 5, 6; m=0) exhibit metallic behavior with a 0 eV band gap. This result is consistent with the findings reported in Refs. [7, 8]. Additionally, another study [11] suggests that for nanotubes with small diameters, the curvature is sufficiently strong to induce rehybridization between the σ- and π-states, leading to band overlap and metallic behavior in SWCNTs. Our results align closely with those reported in Ref. [7]. A systematic analysis of the electronic properties of SWCNT systems reveals that the valence bands primarily consist of carbon s- and p-states, while the conduction bands are predominantly

derived from the p-states of carbon atoms.

3. Conclusion

In this study, we have investigated the electronic properties of single-walled carbon nanotubes (SWCNTs) with chiralities (n=4, 5, 6; m=0) using ab-initio modeling based on Density Functional Theory (DFT). Our results reveal that these SWCNT systems exhibit metallic behavior, characterized by a 0 eV band gap, consistent with prior studies [9, 10]. The analysis of the electronic band structures, total and partial density of states (TDOS and PDOS), indicates that the curvature of the nanotube surfaces plays a critical role in their electronic properties. For nanotubes with small diameters, the strong curvature induces rehybridization between the σ- and π-states, contributing to the metallic character observed in these systems, as noted in previous research.

Furthermore, our results suggest that the valence bands are primarily composed of carbon s- and p-states, while the conduction bands predominantly arise from the p-states of carbon atoms. These findings provide a deeper understanding of the chirality-dependent electronic properties of SWCNTs and underscore the importance of chirality in tuning the material's electronic behavior for potential applications in nanoelectronics, energy storage, and other advanced technologies.

The computational framework developed in this study can serve as a valuable tool for predicting the electronic characteristics of other SWCNT systems with varying chiralities, and could help guide the design of carbon-based nanomaterials for specific technological applications.

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