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ON THE METALLICITY OF SOME CARBON NANOTUBES

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ABSTRACT

Some zigzag and all armchair single-walled carbon nanotubes are believed to behave as metals. However, recent experimental results suggest that only armchair single-walled carbon nanotubes show typically metallic behavior. It has been suggested that metallic zigzag nanotubes are not true metals but small-gap semiconductors. Here we show, through simple quantum chemical calculations, that these zigzag nanotubes exhibit less metallic character than armchair ones because in the former, fewer electrons can flow freely between the valence and conduction bands. Therefore, they can be considered semimetals and not small-gap semiconductors.

INTRODUCTION

Nanotubes (NTs), discovered in 1991, are possible premier building blocks for the coming age of nanotechnology [1-3]. Pure and perfectly cylindrical defect-free carbon NTs are viewed as a conformal mapping of the two-dimensional honeycomb lattice of a single sheet of graphite onto the surface of a cylinder. The helical symmetry of the carbon atoms around the axis of the cylinder is denoted by two integers (m,n) that indicate the number of lattice vectors in the graphite plane used to make the nanotube [4]. For certain values of the couple (m,n) two sub-families of NTs are obtained. For m=n the so-called armchair family of NTs is generated. For the case (m,0) the zigzag family of NTs arises.

It is acknowledged that a relationship exists between the values of the pair (m,n) and the conductivity properties of perfectly cylindrical defect-free carbon NTs. If (n-m)=3t (with t=0,1,2...) the corresponding NTs display metallic behavior. Otherwise, the NTs have semiconducting properties. This indicates that all the armchair and one third of the zigzag NTs should be metallic, but recent experimental evidence has challenged this view.

Lieber et al. used low-temperature scanning tunneling microscopy to characterize the atomic structure and local density of states (DOS) of metallic zigzag and armchair single-walled carbon nanotubes (SWNTs) [5]. Their data recorded for (9,0), (12,0) and (15,0) zigzag SWNTs show the existence of gap-like structures at the Fermi energy. Consequently, they suggested that these metallic zigzag NTs are in fact small-gap semiconductors. Their results also show that isolated armchair SWNTs have neither gaps nor pseudogaps. No clear and simple explanations have been offered to account for these results.

We show here that with the use of Molecular Orbital Theory at the Extended Hückel level (EHT) [6] we can model perfectly the experimental conducting properties of the (m,m) and (m,0) families of isolated SWNTs. The strength of EHT is that it gives a good qualitative picture of the molecular orbitals (MOs) [7, 8 and references therein]. Also, due to the nanotubes' size, the MOs become very similar in energy over a certain range forming wide continuous bands. This contrasts with medium-sized molecules like fullerenes [7, 9]

First, we made use of the concept of "minimal length" to find the lengths of the (5,5) armchair, (9,0) zigzag and (10,0) zigzag NTs, whose study can be safely extrapolated to longer NTs [10]. Notice that here we are dealing with single large molecules and not with a solid [11]. The chosen structures are displayed in Fig. 1 (in the Figs. one unit is equal to one rod of benzene rings rolled in the appropriate way) [12].

Next, the eigenvalues and eigenvectors were obtained, for each structure, using EHT [13]. As the electronic conductance in a NT depends only on its π electrons, the Total Density of States (TDOS) curve must include only those eigenvalues associated with a π MO (the π eigenvalue spectrum). For this purpose a grand total of 1,606 MOs belonging to the three NTs were individually plotted and visually inspected to classify them as π, σ or dangling (the latter are the MOs associated with the unsaturated carbon atoms). Very few cases of mixing were observed, all of them being energetically very far from the Fermi level. For each nanotube the corresponding total π TDOS curves were calculated through a convolution of the π eigenvalue spectrum with a Gaussian function [14].

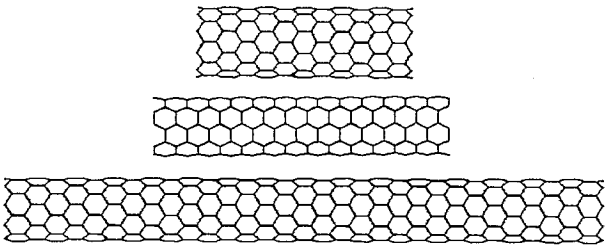

Figure 1. From top to bottom: A (10,0) armchair NT composed of 11 units, a (5,5) zigzag NT composed of 13 units, and a (10,0) armchair NT composed of 31 units.

Fig. 2 shows the π TDOS curve for the (10,0) zigzag nanotube. As expected for a semiconducting molecular system, we observe a gap of about 0.3-0.4 eV between the valence and conduction bands. Knowing that EHT underestimates the energy gap, this result compares well with more sophisticated studies [15].

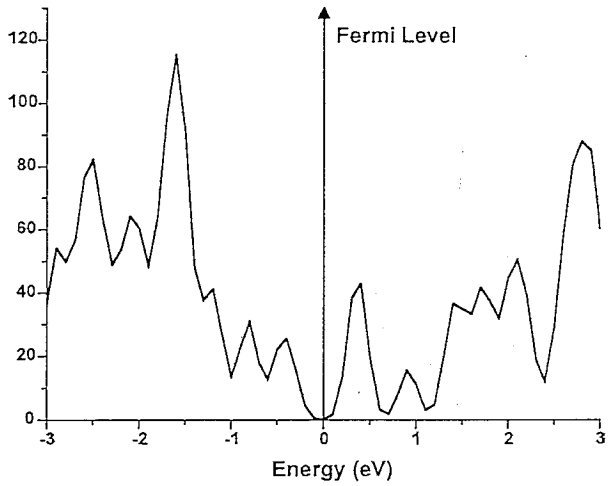

Figure 2. π TDOS curve for the semiconducting (10,0) SWNT.

Fig. 3 shows the π TDOS curve for the (5,5) armchair NT. We can see that there are no impediments for the electrons to flow from the valence band (left side of Fig. 3) to at least all the available states in the conduction band between the Fermi Level and a small pseudogap located at about 0.9 eV. This is congruent with fully metallic behavior.

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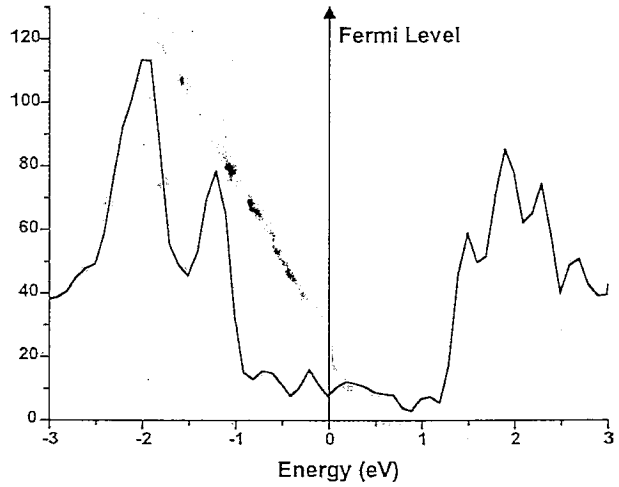

Figure 3. π TDOS curve for the metallic (5,5) SWNT.

Fig. 4 shows the π TDOS curve for the (9,0) zigzag NT. No gap is observed between the valence and conduction bands. Here, and contrarily to the case of the (5,5) NT, the full conduction band is accessible. Nonetheless, only the electrons occupying the states between the Fermi Level and a pseudogap located at -0.6 eV may flow freely towards the conduction band. This smaller number of electrons is the reason for the less metallic behavior of the zigzag SWNTs.

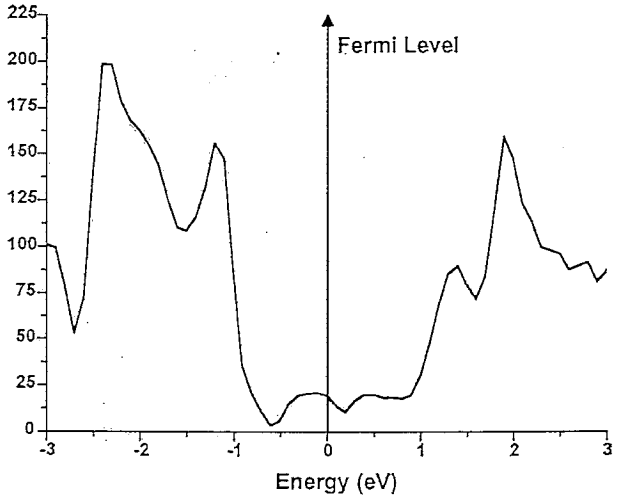

Figure 4. π TDOS curve for the metallic (9,0) SWNT.

We conclude therefore that zigzag SWNTs are not small-gap semiconductors but semimetallic molecular systems. A second conclusion is that, if the Extended Hückel Method is used on large or very large molecular systems it will perform well for certain properties such as chemical hardness and the electronic chemical potential, quantities involved in electron transfer [7].

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12. Due to the rigidity of the NT skeleton, molecular geometries were fully optimized with Molecular Mechanics as provided in the Hyperchem Package (Hypercube, Inc. 1115 NW 4th St. Gainesville, FL 32601 USA).
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