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Semiconductor-to-metal transition of double walled carbon nanotubes induced by inter-shell interaction

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Nuclear magnetic resonance measurements on isotope engineered double walled carbon nanotubes (DWCNT) suggest a uniformly metallic character of all nanotubes. This effect can only be explained by the interaction between the inner and outer shell. Here we study the DWCNTs by density functional theory and inter-molecular Hückel model. We present a study of the density of states of DWCNTs which clearly shows that two layers of semiconducting single walled nanotubes can indeed form a metallic DWCNT in many cases, but not necessarily in every case. For most metallic DWCNTs, a high density of states can be expected at the Fermi level.

1 Introduction

Carbon nanotubes have been intensively studied in the past 15 years due to their high application potential and their rich physics. Single walled carbon nanotubes (SWCNTs), in particular, show fundamental phenomena ranging from e.g. possible superconductivity [1] or Luttinger-liquid state [2] to Peierls distortion [3]. The electronic properties of SWCNTs are known to be fully determined by the (n, m) chiral indices (which essentially define the alignment of the hexagons on the SWCNT surface with respect to the tube axis) [4]. Peapod annealing produced double walled carbon nanotubes (DWCNTs) [5] also possess a number of unique properties such as very long phonon and optical excitation life-times [6].

DWCNTs are interacting systems consisting of two subsystems: an inner and an outer SWCNT. The subsystems are still well defined by their (n, m) chiral indices, but lose some of their identity due to the interaction, as suggested by recent experiments. Nuclear magnetic resonance (NMR) measurements show the extremely surprising result that the DWCNTs have a highly uniform metallic character [7]. This observation contradicts theoretical expectations for SWCNTs, especially in the diameter region of the inner tubes, where curvature induces a secondary gap in non-armchair tubes that should be metallic by simple zone folding approximation [8]. Therefore, these NMR observations can only be explained by the interaction between the inner and outer wall.

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In this work we present the results of our theoretical investigation of inter-shell interaction and its consequences in DWCNTs. We studied 65 different DWCNTs by inter-molecular Hückel (IMH) model [9, 10] and 6 commensurate DWCNTs by first principles density functional theory within the local density approximation (LDA) [11, 12]. Particular attention will be payed to the development of the electronic density of states (DOS).

2 Method

LDA calculations were performed both with a plane wave (VASP [11]) and a localized basis set (SIESTA [12]) package. In the VASP calculations the projector augmented-wave method was applied using a 400 eV plane-wave cutoff energy, while in the SIESTA calculations double-ζ plus polarization function basis set was employed. 16 irreducible *k*-points were used; comparison with test calculations using 31 *k*-points showed this to be sufficient. As these codes use periodic boundary conditions, only commensurate DWCNTs can be studied by them in practice. Otherwise, a model of incommensurate DWCNTs would require huge supercells. An alternate approach to compare the inter-shell interaction in different DWCNTs is the inter-molecular Hückel (IMH) model [9, 10]. In this case the tight binding wave functions originate from the inner and outer tubes (orbital mixing). The tight binding principle can be generalized to apply to both intra- and inter-molecular interactions [13–15], leading to the IMH model [9], which has been successfully applied to study DWCNTs [10] and bundles of SWCNTs [16].

In the IMH calculations, all inner tubes with diameters $d_{\text{inner}} = 0.7 \pm 0.05$ nm were examined, and for each inner tube all outer tubes with diameters $d_{\text{outer}} = d_{\text{inner}} + 0.72 \pm 0.04$ nm were considered yielding a total of 60 different DWCNTs. In addition we have also studied five other DWCNTs which are outside of the aforementioned diameter range, but could still be present in the sample, in order to compare with the LDA calculations. The 6 commensurate DWCNTs studied by LDA were: (4, 4)@(9, 9), (5, 5)@(10, 10), (6, 6)@(11, 11), (7, 0)@(16, 0), (8, 0)@(17, 0), and (9, 0)@(18, 0).

3 Results

We calculated the band structures of the 6 commensurate DWCNTs by LDA. The three armchair@armchair DWCNTs are all metallic, exactly as expected. The (8, 0)@(17, 0) remains a semiconductor, while the other two zigzag@zigzag tubes are metallic. It is important to note, that all zigzag SWCNTs considered were originally semiconducting: the LDA gaps of (7, 0) and (16, 0) were 0.21 eV and 0.54 eV, respectively, while those of (9, 0) and (18, 0) were 0.096 eV and 0.013 eV, respectively [8]. The LDA band gap of (8, 0)@(17, 0) is about 0.2 eV that is much smaller than that of the individual SWCNTs of about 0.6 eV [8].

Figure 1 shows the density of states in the case of the (7, 0)@(16, 0). It can be seen that the Fermi level is shifted into the former conduction band of the (7, 0) tube as a result of charge transfer (CT) between the two layers. The CT is on the order of 0.001 e/atom, which is much smaller than what is usual in e.g. alkali-intercalation experiments. This small CT results in a relatively small shift of the Fermi level, and thus the Fermi level is located very close to the edge of the former conduction band of the (7, 0) tube. Since there is a Van Hove singularity at the edge of the band, this small CT results in a high density of states at the Fermi level, as it can be clearly seen in Fig. 1. A similar result is found for the (9, 0)@(18, 0) DWCNT.

The aforementioned charge transfer occurs universally for all DWCNTs studied [17]. For the 6 commensurate DWCNTs, the CT was determined both from the LDA and the IMH calculations, and good agreement was found. The CT was evaluated for all DWCNTs studied with the IMH method. The direction of the CT is always the same, it is always the inner tube which becomes negatively charged. Furthermore, CT is reduced as the diameter difference of the outer and inner tube increases, exactly as one would expect. The CT density along the tube axis in units of e/Å can be approximately given by the linear formula $-0.028\,\Delta d + 0.219$, which approximately corresponds to a range of 0.0005 to 0.0045 e/atom for the inner wall, and 0.0002 to 0.0024 e/atom for the outer wall [17].

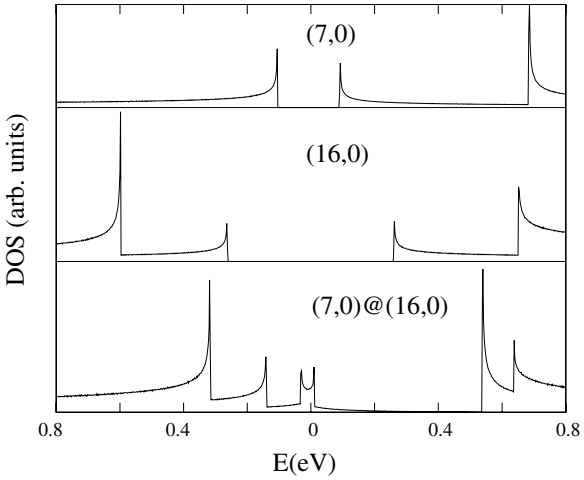

Fig. 1 Density of states of the (7, 0)@(16, 0) DWCNT (VASP), in comparison with density of states found for their subsystems in isolated single geometry (all Fermi levels are shifted to 0 eV).

Based on the results on (7, 0)@(16, 0) and (8, 0)@(17, 0), we expect that the density of states at the Fermi level will be likewise large in nearly all metallic DWCNTs due to the small magnitude of the CT. The only exceptions are those DWCNTs where both the inner and the outer tube is an armchair tube, as in the case of armchair tubes the Van Hove singularities are very far from the Fermi level and therefore it is not expectable to see a large increase of the density of states. Our LDA results for the band structure of the three armchair@armchair DWCNTs show that indeed there is no significant increase of the density of states at the Fermi level.

The CT occurs even in the case of the (8, 0)@(17, 0), which remains a semiconductor, as written above. This may seem surprising at first, but in light of the very apparent orbital mixing it is fairly straightforward. As mentioned above, the band gap of the (8, 0)@(17, 0) is three times smaller than the band gap would be in a model neglecting inter-shell interaction. This decrease of the gap is due to a contraction of the bands, which is a result of hybridization between the orbitals of the inner and outer tubes. Thus, the valance and conduction bands of the (8, 0)@(17, 0) are mixture bands, making it easy to understand why there is CT between the shells when the system is still a semiconductor with a considerable band gap. This also underlines the importance of orbital mixing between the orbitals of the inner and outer shell.

4 Conclusions

We have performed calculations on a large number of double walled carbon nanotubes, using density functional theory and the inter-molecular Hückel model. We have found that the interaction between the layers can lead to a semiconductor-to-metal transition, but not necessarily to a universal metallicity of DWCNTs. We have found that as part of the inter-shell interaction, electrons are transferred from the outer tube to the inner tube in all cases, on the order of 0.001 e/atom. We have found that orbital mixing is a very important part of the interaction between the layers, and in some cases it can greatly reduce the band gap of semiconducting DWCNTs by causing a contraction of the bands. For metallic DWCNTs, we have found that the small magnitude of the CT results in a large density of states at the Fermi level in zigzag@zigzag tubes, and we predict that with the exception of armchair@armchair tubes, all metallic DWCNTs have a high density of states at the Fermi level.

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