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2006 J. Phys.: Condens. Matter 18 5175

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## ***Ab initio* study of F- and Cl-functionalized single wall carbon nanotubes**

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Received 28 November 2005

Published 19 May 2006

Online at [stacks.iop.org/JPhysCM/18/5175](http://stacks.iop.org/JPhysCM/18/5175)

### **Abstract**

First-principles calculations were carried out to study the functionalization of single wall carbon nanotubes by the chemical absorption of F and Cl atoms. Our results confirmed that the band gap of semiconductor zigzag carbon nanotubes is reduced on addition of F or Cl atoms on the walls of the nanotubes. For metallic armchair nanotubes, the doubly degenerate states crossing the Fermi level were separated by the introduction of F or Cl atoms. An additional energy level emerged near the Fermi level, due to coupling between the carbon nanotube and the F or Cl atom. For zigzag nanotubes, charge transfers of  $0.27e$  from the tube to the Cl atom and of  $0.41e$  to the F atom took place, while for armchair nanotubes, the charge transfers from the nanotube to Cl and F are  $0.25$  and  $0.42e$ , respectively. The Cl–C and F–C bond lengths were found to be 2.09 and 1.49 Å, respectively. The systems show semiconducting behaviour when charged with one electron per halogen atom, but remain metallic under hole injection, regardless of the chirality of the carbon nanotubes.

### **1. Introduction**

The functionalization of single wall carbon nanotubes (SWCNTs) through the chemical binding of atoms, molecules or molecular groups has attracted much attention, as it offers a possible way to modify the electronic, chemical, optical and mechanic properties of SWCNTs [1–3]. Experimentally, the functionalization of SWCNTs can be realized by introducing molecules or molecular groups to their open ends or on their walls, through carbodiimide chemistry, or by mixing the SWCNTs with an electrophilic reagent [2–4]. The functionalization dramatically changes the chemical, electronic, and transport properties of SWCNTs and the metal–nanotube contact properties [5–15]. For example, the functionalization of carbon nanotubes by nucleic acid enhanced the reactivity by providing structural support to the

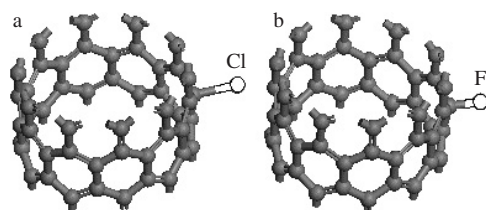
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CNTs and improved the chemical reactivity [5]. Modelling of carbon nanotube Schottky barrier modulation under oxidizing conditions suggested that oxygen molecules increase the potential drop with a negative oxygen charge [9]. The binding of ammonia on carbon nanotubes was mostly electrostatic in nature and very little charge transfer occurred [10]. Theoretically, computational studies based on density functional theory (DFT) have been carried out to investigate the mechanism behind the functionalization of SWCNTs by molecules or molecular groups [15–22]. It was found that the adsorbed molecules or atoms change the  $sp^2$  local hybridization and lead to the formation of  $\pi$ – $\pi$  conjugated bonds at the surface of the SWCNT. However, results of DFT calculations on the effect of oxygen molecules on the properties of CNTs have not been consistent. Calculations based on the local-density approximation (LDA) predicted a finite charge transfer from the carbon nanotube to the physisorbed oxygen molecule [11, 13, 17], while those based on the generalized gradient approximation (GGA) [23–25] and quantum chemistry calculations at the MP2 level [26, 27] suggested that oxygen does not dope the CNT. Available experimental results support the latter and suggest that the main effect of oxygen adsorption is not to dope the bulk of the tube, but to change the work function of the metal contact, even though alkali metals like potassium act as dopants [7, 8]. The discrepancy in the results of DFT calculations could be due to the different forms of exchange–correlation functional and the lack of explicit treatment of van der Waals interactions. Nevertheless, a first-principles method based on DFT does accurately describe chemisorption and produces very reliable results.

Experiments on nanotube functionalization started with the fluorination of SWCNTs [28]. Recently, it was demonstrated by Touhara and Okino that the halogen atoms are chemically absorbed onto the wall of carbon nanotubes, which results in diverse electronic structures [29]. However, there have been few theoretical studies on the functionalization of CNTs by F and other atoms such as Cl. Due to their large electronegativity, one can expect that such atoms will be chemically absorbed on carbon nanotubes and affect the physical properties of the nanotubes. Here, we carried out *ab initio* total energy calculations on the electronic properties of single wall carbon nanotubes with F or Cl attached. Both semiconducting and metallic SWCNTs were considered in our calculations to investigate the effect of the functionalization. Besides the neutral charge state, we also considered charge states which can be important when an external bias is applied in certain applications based on doped semiconducting SWCNTs.

## 2. Computation details

A first-principles method based on DFT [30, 31] and GGA was used to investigate the structural and electronic properties of SWCNTs with F or Cl atoms attached. In our calculations, we used the plane-wave basis pseudopotential method [32] and the CASTEP (CAMbridge Serial Total Energy Package) code [31]. The ionic potentials were described by the ultrasoft non-local pseudopotential proposed by Vanderbilt [33]. The Monkhorst and Pack scheme of  $k$ -point sampling was used for integration over the first Brillouin zone [34]. The Kohn–Sham energy functional was minimized directly using the conjugate-gradient method [35]. Calculations were carried out for a zigzag (10, 0) and an armchair (5, 5) SWCNT (denoted ZZ10 and AC5, respectively). The unit is periodic in the direction of the tube axis, with a cell height ( $c$ ) of 4.24 Å for zigzag tubes and 4.88 Å for armchair tubes. An energy cut-off of 400 eV and ten  $k$ -points along the axis of the tube in the reciprocal space were used in our calculation. Good convergence was obtained with these parameters, and the total energy converged to  $2.0 \times 10^{-5}$  eV/atom. A large supercell dimension, with a wall-to-wall distance of 12 Å, in the plane perpendicular to the tube axis was used to avoid interaction between the carbon nanotube and its images in neighbouring cells.



**Figure 1.** The models of the (a) ZZ10-Cl and (b) ZZ10-F used in our calculation. One F or Cl is attached on the wall of the zigzag (10, 0).

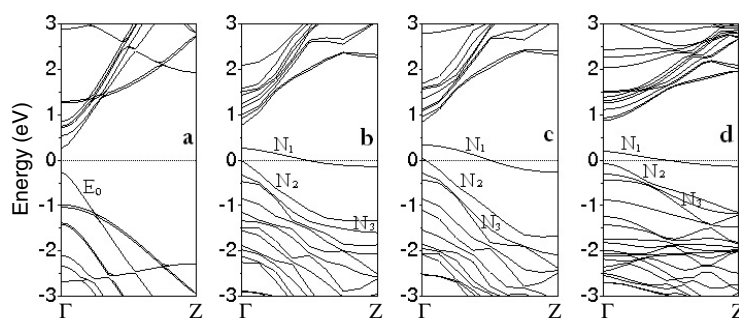
One F or Cl atom was included in the above supercell containing 40 carbon atoms to simulate the functionalization, and it was chemically attached to the wall of the nanotube. Because of the periodic boundary condition in the direction of the tube axis, our model actually corresponds to an infinite single wall carbon nanotube with a row of attached F or Cl atoms separated by  $c$  from each other. Calculation using a larger supercell ( $c \rightarrow 2c$ ) did not change the results noticeably for the F-functionalized ZZ10 nanotube (see below). Therefore, all subsequent calculations were carried out using the smaller supercell. Due to the symmetry of CNT, the C–C bonds are symmetrically equivalent. The choice of carbon atom to which F or Cl is attached should not affect the results of the calculation. The geometry of the SWCNT, with and without the F- or Cl-functionalization, was fully optimized. Figure 1 shows the optimized structure of the Cl (figure 1(a)) and F (figure 1(b)) functionalized zigzag (10, 0) with Cl or F atom attached to the wall. The properties of the carbon nanotubes such as band structure, density of states (DOS) and population analysis were calculated, based on the optimized structures.

### 3. Results and discussion

#### 3.1. F- and Cl-functionalized zigzag (10, 0) carbon nanotube

In the optimized ZZ10-F and ZZ10-Cl systems (figure 1), the local structure around the carbon atom to which Cl or F is attached is slightly distorted. When Cl or F is introduced to the carbon nanotube, one of its p orbitals forms a  $\sigma$  bond with the carbon p orbital which is perpendicular to the tube wall. Thus the carbon atom to which the halogen atom is attached has four  $\sigma$  bonds: three with neighbouring carbon atoms and one with the halogen atom. The local  $\pi$  bonding was distorted after the functionalization. By carefully analysing the bonding around the carbon atom to which the Cl or F is attached, we found that the angles between the Cl–C or F–C bond and the C–C bond fall in the range of  $100^\circ$ – $106^\circ$ . The angles between the C–C bonds near the halogen atom fall in the range of  $111^\circ$ – $116^\circ$ , which were around  $119^\circ$  in the unfunctionalized tube. The C–C bond lengths are within 1.44 and 1.47 Å, which are larger than that in the unfunctionalized tube (1.42 Å). It can be concluded that the local  $sp^2$  hybridization was partially destroyed due to the introduction of Cl or F and a bond was formed between C and Cl or F, which leads to the local deformation and the  $sp^3$  hybridization. The C–Cl and C–F bond lengths are 2.09 and 1.49 Å, respectively. The calculated binding energies are 0.98 and 0.93 eV for Cl and F, respectively (see table 1).

The band structure of the pure zigzag (10, 0) carbon nanotube, which has the  $D_{10h}$  symmetry, is shown in figure 2(a). Most of the energy levels are doubly degenerate, which is a general property of achiral carbon nanotubes due to the rotational point group  $C_n$ . The band structure obtained here is very similar to that in [36]. The pure tube shows a semiconducting



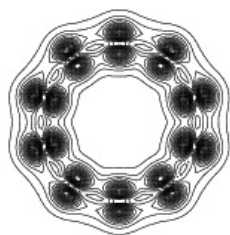
**Figure 2.** (a) Band structure of the zigzag (10, 0) SWCNT near the Fermi level ( $E_F = 0$  eV); (b) band structure of the ZZ10-Cl system; (c) band structure of the ZZ10-F system; and (d) same as (c), but calculated using a larger supercell, with a cell height of 8.48 Å.

**Table 1.** The calculated binding energy, equilibrium distance between the halogen atom and the tube, and the amount of charge transfer from the CNT to the halogen atom.

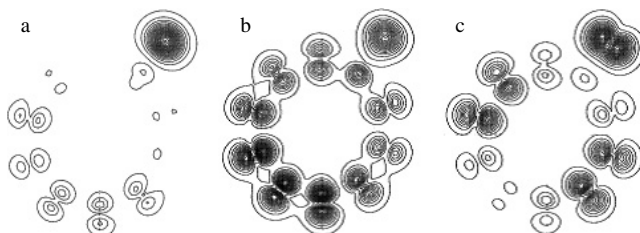
System	Binding energy (eV)	Bond length (Å)	Charge transfer ( $e$ )
ZZ10-Cl	0.98	2.09	0.23
ZZ10-F	0.93	1.49	0.41
AC5-Cl	0.97	2.09	0.25
AC5-F	0.95	1.49	0.42

feature with a band gap of 0.51 eV within GGA. The highest valence band consists of two degenerate bands, denoted  $E_0$  in figure 2(a), which contributes to the  $\pi$  bond extending over the surface of the tube [37]. The bottom of the conduction band corresponds to the extended  $\pi^*$  anti-bonding states. Introducing Cl or F to the tube results in significant changes in the band structure, as can be seen in figure 2. In both F- and Cl-functionalized nanotubes, an energy level crosses the Fermi level ( $E_F = 0$ ). The fine band structure near  $E_F$  shows clearly that the energy levels below the Fermi level split after Cl or F is introduced to the tube. A single occupied molecular orbital (SOMO) is formed upon the addition of a halogen atom, according to radical organic chemistry. The original doubly degenerate state ( $E_0$ ) in the pure tube splits. The energy difference between the two top valence levels is 0.32 eV in the ZZ10-Cl system and 0.34 eV in the ZZ10-F system at the  $\Gamma$  point. The separation of energy levels is due to the reduced symmetry of the system after Cl or F was introduced.

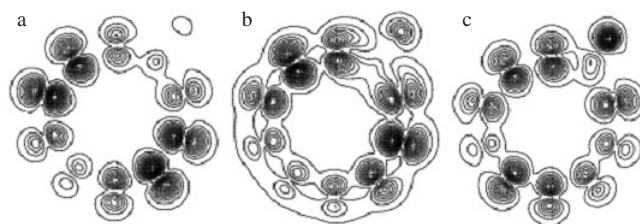
As mentioned above, the dimension of the supercell in the direction of the tube axis is 4.24 Å for the ZZ10 nanotube and 4.84 Å for the AC5 nanotube. There is concern that the F or Cl atoms in neighbouring cells may interact each other. We carefully analysed the electron wavefunction and found that overlap between the wavefunctions of F or Cl atoms in neighbouring cells is negligible near the cell boundary. The finite dispersion of the  $N_1$  state in the band structure of the SWCNT-F or SWCNT-Cl systems (figures 2(b) and (c)) is attributed to interaction between F or Cl atoms and the non-local  $E_0$  state. To double-check this, we repeated the calculation of chemisorbed F on the ZZ10 nanotube using a larger supercell (cell height of 8.48 Å). The calculated band structure is shown in figure 2(d). The only noticeable change is the slight reduction in the width of the  $N_1$  level compared to that shown in figure 2(c). Therefore, it can be concluded that interaction between F or Cl atoms in neighbouring cells is too insignificant to make any difference in the calculated results and all subsequent calculations were performed using supercells which are one unit long in the direction of the tube axis.



**Figure 3.** Electron density of  $E_0$  level in the pure zigzag (10, 0) tube.



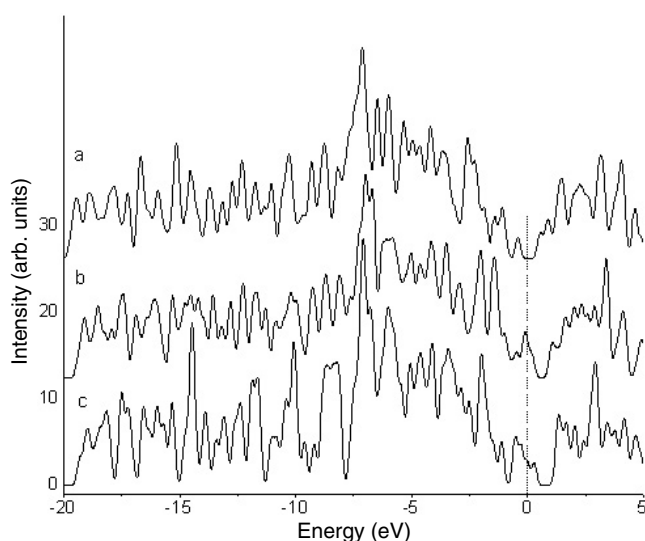
**Figure 4.** Electron density of (a) the  $N_1$  level crossing the Fermi level, (b) the  $N_2$  level, and (c) the  $N_3$  level in the ZZ10-Cl system, respectively (see figure 2(b)).



**Figure 5.** Electron density of (a) the  $N_1$  level crossing the Fermi level, (b) the  $N_2$  level, and (c) the  $N_3$  level in the ZZ10-F system, respectively (see figure 2(c)).

The  $E_0$  state consists of extended  $\pi$  bonding in the pure tube. Figure 3 shows the electron density of this orbital. The extended  $\pi$  bonding characteristics are clearly seen in the figure. Analysis of electron density of the corresponding orbitals in the ZZ10-Cl or ZZ10-F systems reveals the mechanism behind the separation of the doubly degenerate  $E_0$  state and the difference between the two systems. In ZZ10-Cl, the doubly degenerate  $E_0$  state splits into two levels, which interacts with the two p orbitals of Cl.  $N_1$ ,  $N_2$ , and  $N_3$  (shown in figure 2(b)) correspond mainly to one p orbital of Cl (the extension of the p orbital is parallel to the tube axis) (figure 4(a)), the bonding state between the p orbital and the extended  $\pi$  orbital (figure 4(b)) and the anti-bonding state between another p orbital (perpendicular to the tube axis) and the extended  $\pi$  orbital (figure 4(c)), respectively. However, in ZZ10-F,  $N_1$ ,  $N_2$ , and  $N_3$  (shown in figure 2(c)) correspond mainly to one separated  $E_0$  state (figure 5(a)), the anti-bonding state between the p orbital (parallel to the tube axis) and the extended  $\pi$  orbital (figure 5(b)) and the bonding state between the p orbital (parallel to the tube axis) and the extended  $\pi$  orbital (figure 5(c)), respectively.

The calculated total DOS (TDOS) further revealed the splitting of the degenerate states and the expansion of the DOS. Figure 6 shows the TDOS of the pure zigzag nanotube (curve a), the TDOS of the ZZ10-Cl (curve b), and the TDOS of the ZZ10-F (curve c). Different



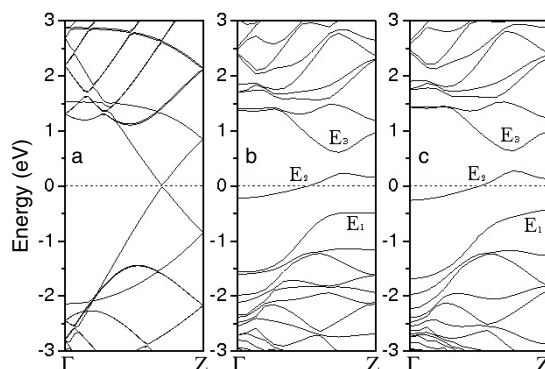
**Figure 6.** Calculated total DOS of (a) the pure zigzag (10, 0) nanotube, (b) ZZ10-Cl, and (c) ZZ10-F. The Fermi level (dotted line) is at 0 eV.

features can be seen between the TDOS of the ZZ10-Cl or the ZZ10-F systems and that of the perfect SWCNT. When the F or Cl atom is introduced to the tube wall, a peak in the TDOS arises near the Fermi level and the energy gap is reduced. This is also seen in the band structure (figures 2(b) and (c)). The Cl or F possesses an unpaired electron, which participates in hybridization with orbitals of the C atom when it is attached to the tube. This results in the formation of an acceptor level and an enhancement in the conductivity of the CNT, as indicated in the band structures (figures 2(b) and (c)). Changes in the TDOS due to F- or Cl-functionalization can also be seen in other energy ranges, but they are minor. The main features in the TDOS of the pure tube remain in the TDOS of the ZZ10-Cl or ZZ10-F systems, due to the fact that the TDOS in these regions is dominated by the carbon states.

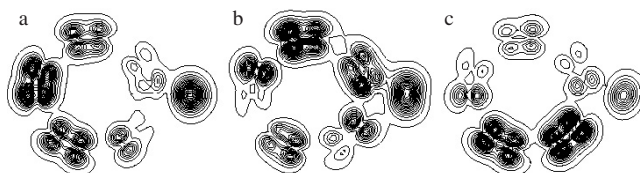
The chemical absorption of an atom is different from the physisorption of a molecule because a chemical bond is formed between the halogen atom and a carbon atom of the carbon nanotube. When Cl or F is chemically absorbed onto the tube wall, electrons are transferred from the tube to the atom due to its large electronegativity. From the Mulliken population analysis, we found a charge transfer of  $0.27e$  per Cl atom and  $0.41e$  per F atom, respectively, for a zigzag (10, 0) nanotube (table 1).

### 3.2. Cl- and F-functionalized armchair (5, 5) carbon nanotubes

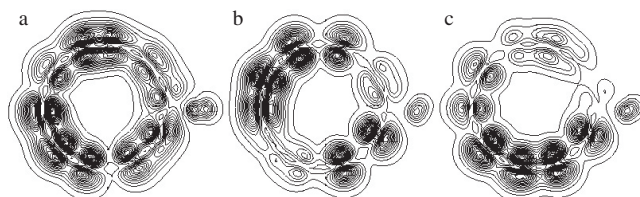
The distortion of geometry in AC5 induced by the Cl- or F-functionalization is similar to that of Cl- or F-functionalized zigzag (10, 0) nanotubes. Figure 7(a) shows that the pure armchair (5, 5) carbon nanotube is metallic. Introducing Cl to the tube results in significant changes in the band structure, as can be seen in figure 7(b). The fine band structure near  $E_F$  shows clearly that the energy levels below the Fermi level split after Cl is introduced to the tube and the doubly degenerate states at the Fermi level are separated. Introducing an F atom to the pure tube results in similar effects as that induced by Cl-functionalization, as shown in figure 7(c). The separation of energy levels is due to the reduced symmetry of the system after the Cl or F atom was introduced. Figures 8 and 9 show the electron densities of the



**Figure 7.** Band structures of (a) the unfunctionalized armchair (5, 5) SWCNT, (b) the AC5-Cl system, and (c) the AC5-F system near the Fermi level ( $E_F = 0$  eV).



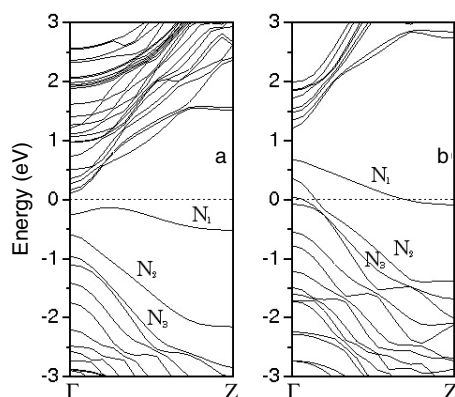
**Figure 8.** Electron densities of (a) the  $E_1$  level crossing the Fermi level, (b) the  $E_2$  level, and (c) the  $E_3$  level in the AC5-Cl system, respectively (see figure 7(b)).



**Figure 9.** Electron densities of (a) the  $E_1$  level crossing the Fermi level, (b) the  $E_2$  level, and (c) the  $E_3$  level in the AC5-F system, respectively (see figure 7(c)).

energy levels  $E_1$ ,  $E_2$ , and  $E_3$  (shown in figures 7(b) and (c)) near the Fermi level in the AC5-Cl and AC5-F systems, respectively. For AC5-Cl,  $E_1$ ,  $E_2$ , and  $E_3$  correspond mainly to the extended  $\pi$  orbital (figure 8(a)), the bonding state between one extended  $\pi$  bonding state and the p orbital of a Cl atom (perpendicular to the tube axis but parallel to the tube wall) (figure 8(b)), and the extended  $\pi^*$  anti-bonding state (figure 8(c)), respectively. For the AC5-F system,  $E_1$ ,  $E_2$ , and  $E_3$  correspond mainly to the anti-bonding state between the p orbital of an F atom (perpendicular to the tube wall) and the extended  $\pi$  orbital (figure 9(a)), one extended  $\pi$  bonding state (figure 9(b)), and the extended  $\pi^*$  anti-bonding state (figure 9(c)), respectively, which are different from those of ZZ10-F. It was found that  $0.25e$  per Cl and  $0.42e$  per F were transferred from the nanotube to the halogen atom, respectively, similar to those in ZZ10-Cl and ZZ10-F. The Cl-C and F-C bond lengths are the same as those in ZZ10-Cl and ZZ10-F, and the binding energies are also quite similar (see table 1).





**Figure 10.** Calculated band structures of (a) the negatively charged and (b) the positively charged ZZ10-F systems. The Fermi level (dotted line) is at 0 eV.

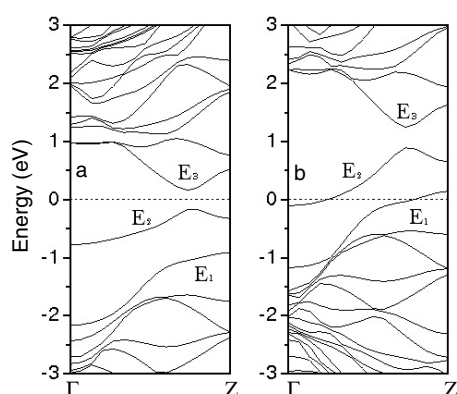
### 3.3. Charged F-functionalized carbon nanotubes

In certain potential applications, an external bias may be applied to devices based on doped nanotubes. Therefore, charge states of the F- or Cl-functionalized nanotubes are of interest. Here, we investigated the charge states ( $\pm e$ ) of the F-functionalized ZZ10 and AC5 nanotubes. The calculated band structures for the charged F-functionalized zigzag carbon nanotube are shown in figure 10. The charge neutral state of ZZ10-F is metallic, because the  $N_1$  energy level (figure 2(b)) is occupied by one electron (the total number of electrons in the neutral system is odd). Adding one electron to the system fills this energy level and results in a semiconducting system. On the other hand, the hole injection does not change the metallic behaviour of the ZZ10-F system due to the overlap between the  $N_1$  band and those below it. From the Mulliken population analysis, we found a charge transfer of  $0.24e$  from the carbon atom to F. About 23% of the injected electron are located at the F atom, and the remaining negative charges are almost equally distributed among the carbon atoms, except for the F-attached atom in the unit cell. Similarly for the hole injected ZZ10-F,  $0.26e$  was transferred to F from the carbon atom to which it is attached, and another  $0.1e$  was transferred from other carbon atoms to the F atom. The positive charges are almost equally distributed among the carbon atoms, except for the F-attached atom in the unit.

Similar effects were found for the charged AC5-F system. The negatively charged ( $-e$ ) system becomes semiconducting, while the positively charged ( $+e$ ) system remains metallic, as shown in figure 11. The charge distribution and transfer in the charged AC5-F system are similar to those in the charged ZZ10-F system.

## 4. Conclusions

In summary, using first-principles calculations, we have carried out a systematic investigation of the functionalization of SWCNTs by F and Cl atoms. Our results show that attachment of F or Cl atoms on the walls of a SWCNT and charge injection into the functionalized systems gave rise to significant changes in the electronic properties of the SWCNTs. For semiconducting nanotubes, such as zigzag (10, 0), an acceptor level was found after the Cl- or F-functionalization, which comes mainly from the interaction between the p orbitals of the doping atom and carbon atom. The interaction between the tube and halogen atom makes the degenerate levels in the pure CNT split. For a metallic nanotube, such as the armchair (5, 5)



**Figure 11.** Calculated band structures of (a) the negatively charged and (b) the positively charged AC5-F systems. The Fermi level (dotted line) is at 0 eV.

nanotube, the Cl- or F-functionalization also results in splitting of the degenerate states. But the systems remain metallic, with an energy level crossing the Fermi level and a finite electron density at the Fermi level. The negatively charged systems, with one electron per halogen atom, show semiconducting behaviour. The additional charge occupied the half-filled energy level, leading to a completely filled valence band and an empty conduction band. The hole-charged systems, with one hole per halogen atom, remain metallic. Based on the results of our calculations, it can be expected that the functionalization of carbon nanotubes by halogen atoms and charging can be an effective way of modifying the electronic properties of semiconducting SWCNTs and can be potentially useful.

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