"Electronic properties of double-walled carbon nanotubes (DWNT) and the effect of functionalization"

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Abstract

Although promising for many electronic applications, further understanding of carbon nanotubes systems are required for practical designs. A difficulty currently hindering further development in this field is the considerable degradation of transport properties in a single-wall carbon nanotube (SWCNT) when it is subjected to ambient conditions or functionalized. Double-wall carbon nanotubes (DWCNT) could solve this problem, by allowing the outer tube to be functionalized while the inner tube would retain a pristine structure and it's promising electronic properties. However, our understanding of interactions between the tubes and their consequences on the system's electronic properties is still incomplete. In this presentation, we investigate those interactions using density-functional theory (DFT) calculations. In particular, we investigate separately the effects of structural deformations, Fermi energy realignment and electronic orbital overlap on the band structure of DWCNT. The e...

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Electronic properties of double-walled carbon nanotubes (DWNT) and the effect of functionalization

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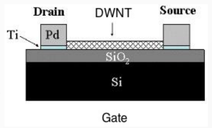
Why study DWNT?

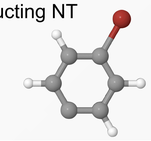
They are promising candidates for field effect transitors (FETs) :



- external tube can be functionalized (easy manipulation)
- internal tube retains pristine structure (good electronic properties)

The present work focus on semiconducting DWNT, since they are those of interest for FETs.

They should be formed by two semiconducting NT (S@S DWNT)



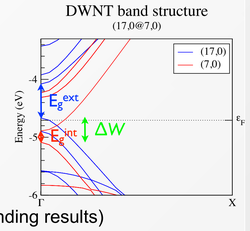
Two aspects of this system studied :

1. effect of wall interaction
2. the effect of functionalization with phenyls

Part 1 : Wall interaction in DWNT

Effect of NT curvature known:

- work function *W* of NT depends on curvature
- difference of curvature in DWNT leads to difference of work function ΔW
- ΔW can leave S@S DWNT semiconducting or make them metallic [1-4] (ab initio and tight binding results)

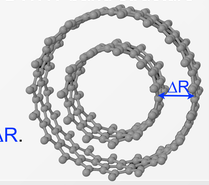


Are there effects of wall interaction on DWNT band structure beyond the difference of curvature ?

We assess the effect of :

1. Structural deformation
2. Electronic interactions

with respect to the interwall distance ΔR.



Method

Structures optimisations and band structures calculations were done using the density functional theory (DFT) as implemented in the Abinit package [5].

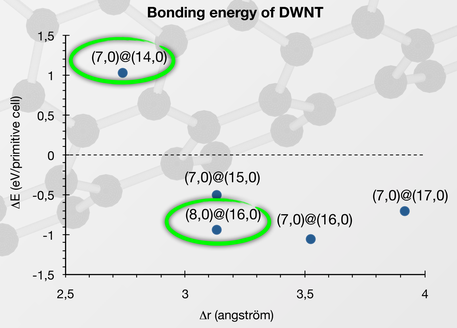
In these calculations, we used :

- the local density approximation (LDA)
- a 35 Ha cutoff for the plane wave basis set
- a 7 angström distance between tubes (to prevent interaction between the tubes)
- a 1 1 6 k-points grid

Only (n,0)@(n,0) DWNT (i.e. made of two zigzag NT) were simulated, to keep the calculation time manageable.

Bonding energy of DWNT

To select realistic interwall spacing ΔR for band structure calculations, we studied the bonding energy ΔE dependance on ΔR.



Bonding energy of DWNT (continued)

The optimal interwall diatance is $\Delta R \sim 3.5$ angström.

A distribution of DWNT around this value is expected in syntesised samples.

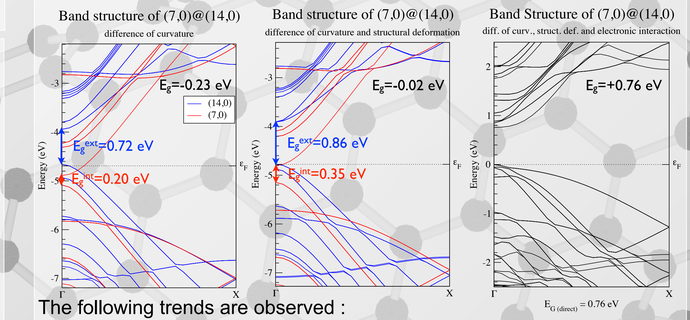
Therefore, to assess the effect of a strong but realistic wall interaction, we study the band structure of a (8,0)@(16,0) DWNT.

We also study a (7,0)@(14,0) DWNT, to assess the effect of extreme wall interaction.

Band structure : (7,0)@(14,0) DWNT

We calculated different band structures to assess the impact of :

1. Difference of curvature only (through the difference of work function ΔW)
2. Difference of curvature and structural deformation (due to the pressure each wall exerts on the other)
3. Difference of curvature, structural deformation and electronic interaction between the walls



The following trends are observed :

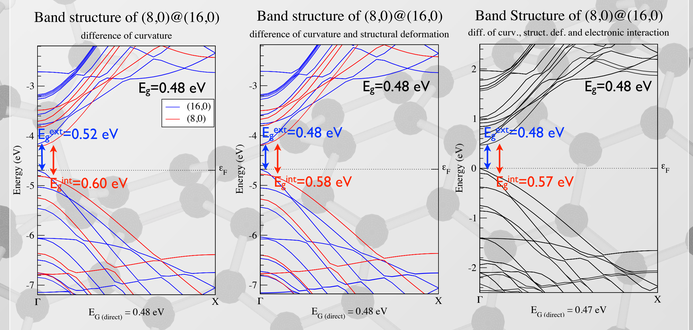
- Inner and outer NT gaps increase when they are deformed from their isolated to their DWNT structure
- electronic interactions open a substantial gap

Therefore, to accurately describe the band structure of small ΔR DWNT, structural deformations and electronic interactions must be considered.

In particular, describing the DWNT band structure by a superposition of the constituent SWNT band structures (which amount to considering the difference of curvature only) leads to qualitatively wrong results.

Band structure : (8,0)@(16,0) DWNT

The following band structures were obtained for a small but realistic interwall spacing (ΔR = 3.1 angström) :



The effect of both structural deformation and electronic interaction are much smaller than the effect of difference of curvature for a bonded tube.

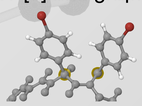
Therefore, given the DWNT is bonded, it's band structure can be well approximated by a superposition of the constituent SWNT band structure with the proper Fermi level shift.

Part 2 : Effect of functionalization

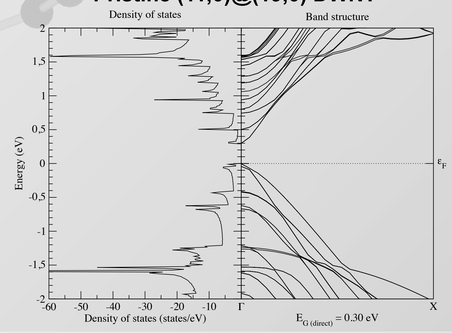
We assess the impact of functionalization with bromo-phenyls on the band structure of (11,0)@(19,0) DWNT.

The most stable configurations on (5,5) DWNT [6] and graphene [7] is studied :

the para configuration (ΔE=-1.51 eV/pair on graphene).

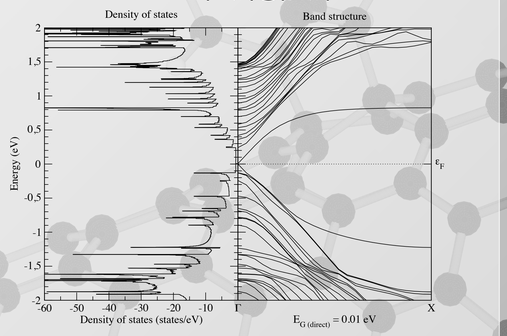


Pristine (11,0)@(19,0) DWNT



Effect of functionalization (continued)

Functionalized (11,0)@(19,0) DWNT



Upon functionalization with one pair of bromo-phenyls per primitive cell, the electronic properties of the DWNT change substantially :

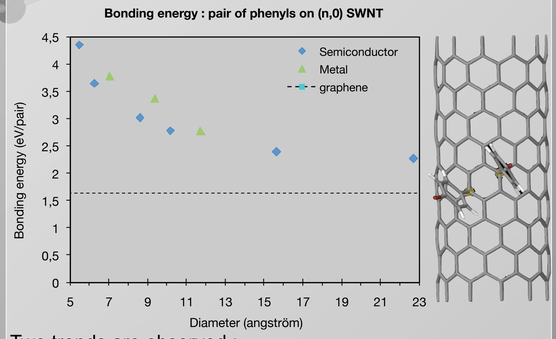
- Two new bands, associated with the phenyl groups, appear
- They induce a small density of states in the gap that nearly makes the DWNT metallic

Bonding energy of phenyls

We now assess which DWNT are most functionalized when a mixture of chiralities is processed.

We assume the bonding energy depends most on the tube diameter and it's metallic or semiconducting behavior and not on the details of it's chirality or it's simgle-walled or double-walled nature.

Therefore, using ONETEP [8], we study the bonding energy of isolated pairs of bromo-phenyls on zigzag SWNT in the para configuration as a function of the tube diameter and of the presence of a gap.



Two trends are observed :

1. The binding energy drops for increasing diameter(tends to graphene value)
2. The bonding is stronger for metallic tubes than for semiconducting tubes.

Conclusion

The band structure of DWNT is well approximated by a superposition of the constituent SWNT band structures for bonded DWNT.

The functionalization of semiconducting DWNT with bromo-phenyls seems to induce a small density of states in the gap.

Functinalization of NT with phenyls is more stable for :

- small NT diameters
- metallic NT

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