Ab initio Calculations of the electronic properties in the SWCNT (4,4)

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Abstract

We have made calculations of the structural and electronic properties of a carbon nanotube "armchair" (4.4) with the functional theory density in the generalized gradient approximation (GGA) using the code SIESTA. The relaxed geometry actually shows a structure whose lengths and bond angles differ from the configuration of the graphene rolled sheet. The electronic band structure along with the density of states effectively confirms that this is a metallic nanotube.

Resumen

Nosotros hemos hecho calculos de las propiedades estructurales y electrónicas de un nanotubo de carbono “armchair” (4,4) con la teoria del funcional de la densidad en la aproximación de gradiente generalizado (AGG) utilizando el codigo SIESTA. La geometría relajada realmente muestra una estructura cuyas longitudes y ángulos de enlaces difieren con respecto a la configuración de la hoja de grafeno enrollado. La estructura de bandas electrónicas junto con la densidad de estados confirman efectivamente que éste nanotubo es metálico.

Introduction

Continued improvements in computational power, as well as, the appearance of new methods that allow scaling linearly with the number of atoms of the system, makes it possible to study the nanosystems with hundreds of atoms such as nanotubes. One method that has had more success in a recent time has been the SIESTA thanks to its good balance between accuracy and computational cost (Soler et al, 2002). Among the more notable features of the method is the use of minimum bases, making it a very efficient method, keeping a good convergence (Artacho et al, 1999).

The system under study in this paper to have 80 atoms, and therefore diagonalization (wich is an order N^3 operation) of the Hamiltonian is feasible and competitive with an order-N technique. We have used

diagonalization in this paper.

In this work, we present first-principles calculations of the structural and electronics properties of a SWCNT (4,4).

Computational Scheme

Ab initio calculations were performed using the code SIESTA within the generalized gradient approximation (GGA) as parametrized by Perdew-Burke-Ernzerhof. A double zeta basis plus polarization orbitals (DZP) was used for the valence electrons. For that basis, cuttof radii of 4.994 a.u for the orbital *s* and 6.254 a.u for the orbital *p* were used, as determined from an energy shift of 50 meV by localization (Artacho et al, 1999) and (Junquera et al, 2001). The pseudopotential that we used is similar to that employed by Javier Junquera (Junquera et al, 2001). It is generated using a GGA functional with partial core correction, a valence reference configuration: 2s2 2p2 3d0 4f0 with Cutoff radius: 2s 1.25 Bohr, 2p 1.25 Bohr, 3d 1.25 Bohr and 4f 1.25 Bohr was used.

In order to avoid interaction between the images a cell unit with 16 Å in the directions *x* and *y,* perpendicular to the axis of the tube was used, although with 12 Å it had been sufficient (view figure 1). Integrations in *k* space were performed over 51 *k* points in the k_z direction. Real-space integrations were done in a grid with a cutoff of approximately 150 Ry.

The atomic positions were relaxed by a conjugate gradient minization until the forces on the atoms were less than 0.04 eV/ Å. The energy was minimized and the structure relaxed for diferent values of the lattice constant along the tube axis. This procedure allows us determine the most stable lattice constant along the tube.

Results

In figure 2 the results of the relaxations are shown together with the parameters published by Daniel Sánchez-Portal et al. (1999) and the reported values were done with LDA. Important changes in the values of the geometric parameters are not observed.

The electronic band structures were calculated using the relaxed geometries described previously. In

the same way, the density of electronic states (DOS) was calculated. DOS is broadened by using the Gaussian-distribution function with the width of 0.02 eV. The results are show in figure 3. According to the Zone folding approach all armchair nanotubes are metallic (Saito et al, 1992). Our results confirm this behavior for the (4,4) armchair carbon nanotube. The zone-folding method predicts for this system no splitting due to the trigonal warping effect (Saito et al, 2000), being as small ΔE_{11} as approximately 10^{-4} eV for our system. Despite, the *ab initio* results show that spliting is much greater. A splitting in the E_{11} and E_{22} transitions of 0.1 and 0.3 eV are observed, respectively.

On the other hand, the obtained values for E_{11}, E_{22} and E_{33} transitions are very much greater than the values obtained by zone folding method (view table 1). A experimental value for E_{11} energy is show on (7,7) carbon nanotube. This value is comparable to the result obtained by means of the ab initio calculations. The transition energies determine the conditions for resonant Raman scattering in nanotubes.

The zone-folding method gives reasonable predictions for the band structure and the optical transition energies for the values of the radii wich are larger than 6 Å. For narrow nanotubes, there can be significant curvature corrections to the zone-folded bands (Popov, 2004).

Acknowledgments

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References

Artacho E, Sánchez-Portal D, Ordejón P, García A, Soler JM, (1999), Linear-Scaling ab-initio Calculations for Large and Complex Systems, *Phys. Stat. Sol., 215*, 809-817.

Fantini C, Jorio A, Souza M, Strano M, Dresselhaus MS, Pimenta MA, (2004), Optical Transitions Energies for Carbon Nanotubes from Resonant Raman Spectroscopy Enviroment and Temperature

Effects, *Phys. Rev. Lett., 14*, 147406-1 – 147406-4.

Hulman M, Pfeiffer R, Kuzmany H, Raman spectroscopy of small-diameter nanotubes, *N. J. Phys.*, *6*, 1-18.

Junquera J, Paz O, Sánchez-Portal D, Artacho E, (2001), Numerical atomic orbitals for linear-scaling calculations, *Phys. Rev. B, 64*, 235111-1 – 235111-9.

Popov VN, Curvature effects on the structural, electronic and optical properties of isoleted single-wall carbon nanotubes within a symmetry-adapted non-orthogonal thight-binding model, *N. J. Phys., 6*, 1-17.

Saito R, Dresselhaus, Dresselhaus MS, (2000), Trigonal warping effect of carbon nanotube, *Phys. Rev. B, 61,* 2981-2990.

Saito R, Fujita M, Dresselhaus G, Dresselhaus MS, (1992), Electronic structure of chiral graphene tubules, *Appl. Phys. Lett., 60*, 2204-2206.

Sánchez-Portal D, Artacho E, Soler JM, Rubio A, Ordejón P, (1999), Ab initio structural, elastic, and vibrational properties of carbon nanotubes, *Phys. Rev. B*, *59*, 12678-12688.

Soler JM, Artacho E, Gale JD, García A, Junquera J, Ordejón P, Sánchez-Portal D, (2002), The SIESTA for ab-initio order-N materials simulations. *J. Phys: Condens. Matt., 14,* 2745-2779.

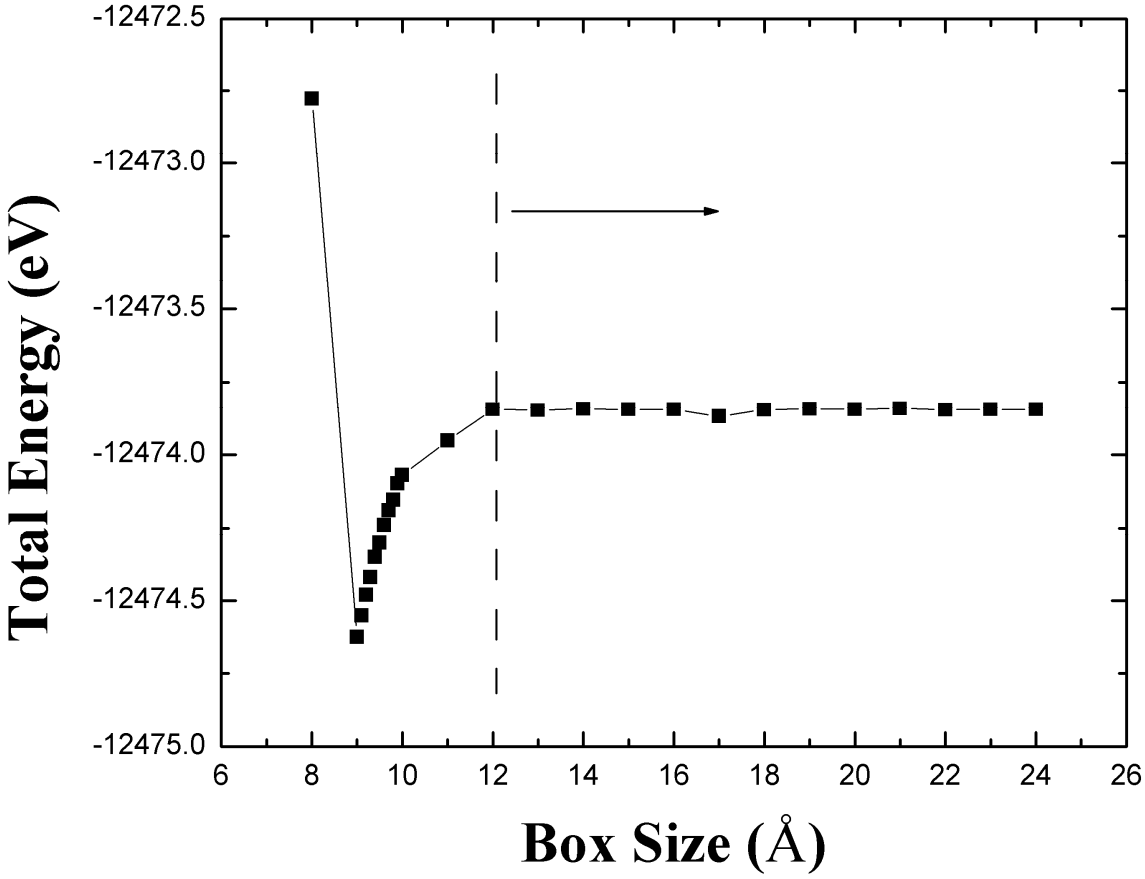
-12472.5
-12473.0
-12473.5
-12474.0
-12474.5
-12475.0
Total Energy (eV)
6
8
10
12
14
16
18
20
22
24
26
Box Size (Å)

Fig. 1

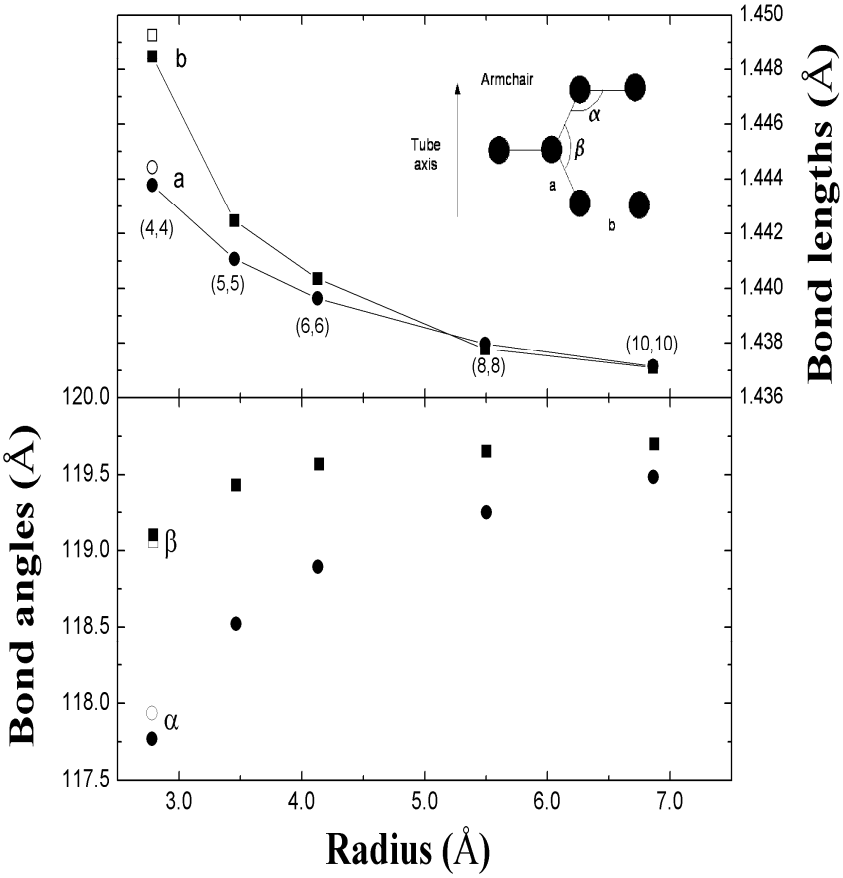
Bond lengths (Å)
Bond angles (Å)
Radius (Å)
b
a
(4,4)
(5,5)
(6,6)
(8,8)
(10,10)
Armchair
Tube axis
α
β
a
b
1.450
1.448
1.446
1.444
1.442
1.440
1.438
1.436
120.0
119.5
119.0
118.5
118.0
117.5
3.0
4.0
5.0
6.0
7.0

Fig. 2

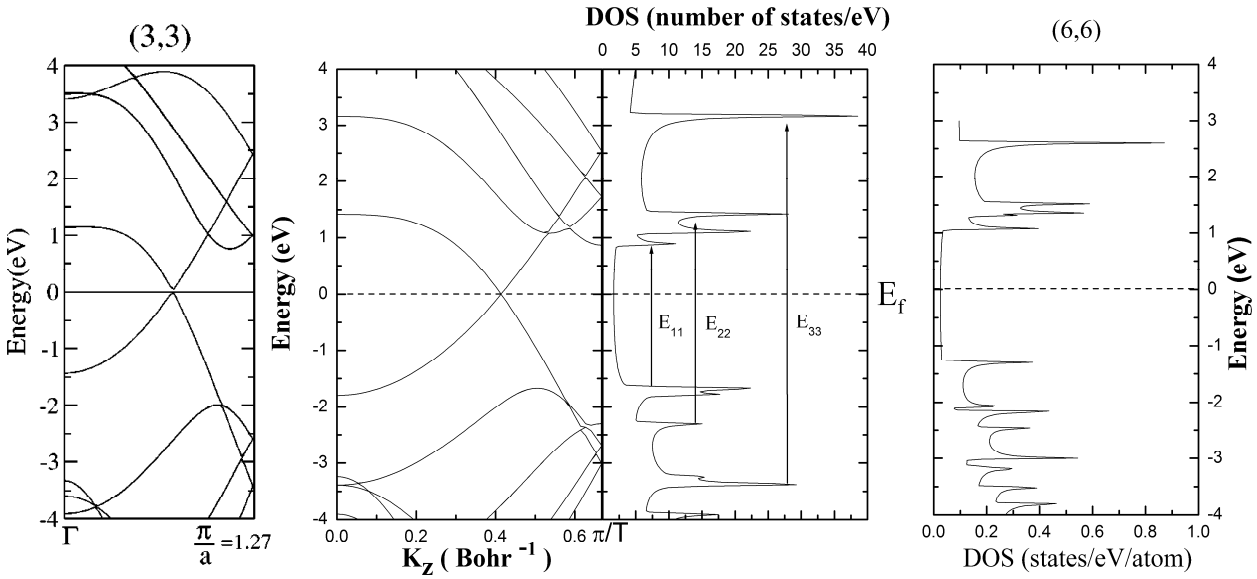
(3,3)
DOS (number of states/eV)
(6,6)
Energy(eV)
Energy (eV)
Γ
π/a =1.27
K_Z (Bohr -1)
π/T
E_f
E11
E22
E33
DOS (states/eV/atom)

Fig. 3

Table 1

	E_{11} (eV)	**E_{22} (eV)**	**E_{33} (eV)**
This work	2.6	3.6	6.5
Zone folding[§]	4.5	9.1	13.5
Experimental[*]	2.43		

§ (Hulman et al., 2004)

***** Experimental E_{11} obtained by Resonance Raman Spectroscopy for (7,7) carbon nanotube. The accuracy is ± 10 meV (Fantini et al., 2004).

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