Density-Functional-Theory Calculation of Semiconducting Carbon Nanotubes under an External Electric Field

Li-Gan Tien[a] (田力耕), Tsong-Ming Liaw[b] (廖聰明), Feng-Yin Li[c]* (李豐穎), Sheng-Hsien Lin[d] (林聖賢), Ming-Hsien Lee[e] (李明憲) and Steward Clark[f]

[a]*National Center for High-Performance Computing, Hsinchu 300, Taiwan, R.O.C.*
[b]*Computing Centre, Academia Sinica, Taipei 115, Taiwan, R.O.C.*
[c]*Department of Applied Chemistry, National Chi-Nan University, Puli, Nantou 545, Taiwan, R.O.C.*
[d]*Institute of Atomic and Molecular Sciences, Academia Sinica, P.O. Box 23-166, Taipei 106, Taiwan, R.O.C.*
[e]*Department of Physics, Tamkang University, Tamsui, Taipei County 251, Taiwan, R.O.C.*
[f]*Department of Physics, University of Durham, Durham, United Kingdom*

We investigate the structure change of semiconducting carbon nanotubes under an external electric field with density functional theory. It is shown that the shape of the nanotube remains cylindrical and the length of the nanotube is also the same, even under a strong electric field. The only change observed is the diameter of the nanotube. It increases along with the increase of the applied electric field.

Keywords: Carbon nanotube; DFT; Semi-conducting; External electric filed.

Since the discovery of carbon nanotubes in 1991,[1] intense research interest has been focused on their remarkable properties, such as high mechanical stiffness and strength.[2] A single-walled carbon nanotube (SWNT) can be metallic, semiconducting or semimetallic, depending on its chirality.[3] Utilization of these properties has led to several important applications such as scanning probes,[4,5] electron field emission sources,[6] and nanoelectronic devices.[7-9] One of the most important findings of SWNT research is that the current in semiconducting single-walled carbon nanotubes (s-SWNTs) can be switched by an external electric field, which allows these s-SWNTs to be used as a channel of field-effect transistors (FETs).[7] Several groups have demonstrated such functional FETs successfully[7-11] and encouraged calculations of their electronic structures such as energy bands, density of states, etc., which have been accomplished, and now an extensive literature exists.[12] The electronic structures of these s-SWNTs under an external electric field have been also calculated theoretically.[13-15] So far, the previous theoretical studies focus on electronic structure change of the s-SWNTs under an external electric field. However, their atomic displacements generated by the electric field effect will definitely influences their electronic structures. The question then arises of what the magnitude of these atomic displacements will be when the switching voltage is applied. Here, we employ *ab initio* quantum calculations to model s-SWNT and address some of these issues.

In this study, we considered a single-wall (10,0) nanotube, modeled by 8 layers of carbon rings (80 carbon atoms) along the tube axis with a periodical boundary condition. In order to facilitate the computation, we place the zigzag (10,0) nanotube in the center of a rectangular unit cell with the tube axis along the c axis. The cell dimensions are $\boldsymbol{a} = \boldsymbol{b} = 20$ Å and $\boldsymbol{c} = 8.2579$ Å. Density functional theory calculations were performed with CASTEP 4.2 code.[16,17] Except where explicitly mentioned, the typical calculation setting is as follows. The calculations were done with geometry optimization in a generalized gradient approximation (GGA)[18,19] in an IBM P690 with 32 CPUs. A constant external electric field is applied to the tube from the direction of the $\boldsymbol{a}$ axis. All the elements of the unit cell are movable except the shape of the cell and the length of $\boldsymbol{a}$ and $\boldsymbol{b}$ axes. The fast-fourier-transform (FFT) grid is set to be $90 \times 90 \times 36$ and we expand the valence electronic wavefunctions in plane waves up to 240 eV cutoff. The nuclei and core electrons are represented by ultrasoft pseudopotentials. Besides the valence bands, we have added 12 extra bands to represent the conduction bands. In order to simulate the s-SWNT under an external electric field, we add an electric potential to the unit cell in the Hamiltonian. The magnitude of the potential linearly decreases from the 10 Å of $\boldsymbol{a}$ axis to -10 Å so that the nanotube in the center feels the constant electric field with preset voltage from the direction

Special Issue for the Second Worldwide Chinese Theoretical and Computational Chemistry Conference

Table 1. The Band Gap and the Diameter of the Zigzag (10,0) Nanotube under Various External Electric Fields

External field (V)	Gap (eV)	Diameter (Å)	*Change in diameter (Å)
0	0.4	7.926	0
5	0.4	7.936	0.010
10	0.4	7.966	0.040
15	0	8.108	0.182
25	0	8.246	0.320

* The fourth column is generated by subtracting the diameter under the external electric field from the unperturbed diameter.

of the ***a*** axis only.

We performed geometry optimization calculation on a zigzag (10,0) nanotube with an external electric field ranging from 0 to 25 volts. The results are summarized in Table 1. From Table 1, it can be understood that the band gap is switched off when the external electric field is somewhere between 10 to 15 V in our calculation. Before the band gap is diminished, the gap remains constant at about 0.4 eV. This value is different from the result found in Reference 13; the band gap of the unperturbed (10,0) nanotube is reported as 0.8 eV. The band structures of the tube unperturbed and under external electric field with 15 V are shown in Fig. 1 for comparison. Interesting phenomena are observed during the process of calculations. Unlike intuitive prediction, there is no obvious distortion in the shape of the nanotube and it remains cylindrical even though we applied the electric field only from the ***a*** axis (see Fig. 2 for detail). The length of the ***c*** axis also remains the same as that in the unperturbed one, but there is a slight change in the diameter of the nanotube when the electric field is applied. We found that the diameter of the tube increases as the electric field is applied, and the magnitude of the diameter increase becomes larger as the electric field increases.

In conclusion, we have demonstrated successfully using the DFT method, in particular the first time in CASTEP code, to study the optimal structure of a zigzag (10,0) nanotube under an external electric field. The results show that the shape of the nanotube remains cylindrical and the length of the nanotube also remains the same under the external electric field. The only change observed is the diameter of the nanotube. It increases along with the increase of the applied electric field. The applied electric gradient in this report is indeed too large to be realized in a laboratory. With available technology, the electric field, at most, reaches above. 1.7 MV/cm.[10] Recently IBM developed p-type and n-type carbon-nanotube field-effect transistors, wherein the gate and nanotubes were separated by about 150 nanometers, which are comparable to traditional silicon dioxide of field-effect transistors.[11] Now there is a lot of effort devoted to shrinking the gate oxide of carbon-nanotube field-effect transistors to 2 nm, and the electric gradient of magnitude used in our calcu-

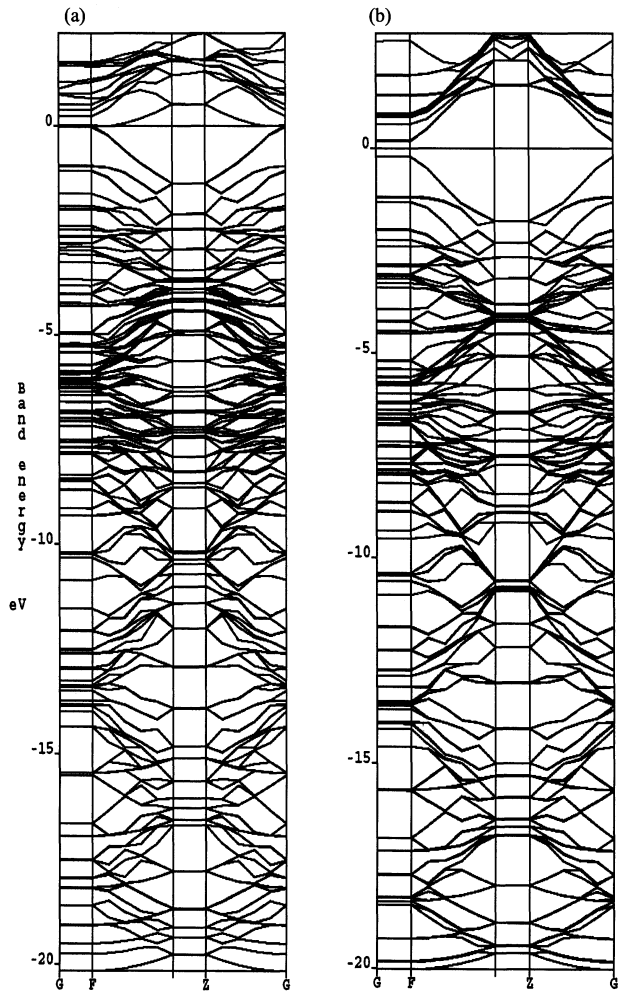

Fig. 1. The band structures of a zigzag (10,0) nanotube. (a) The band structure of the nanotube under electric field with 15 V. The zero of band energy indicates the fermi level. (b) The unperturbed band structure.

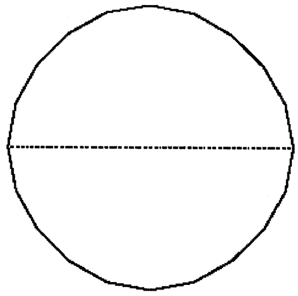

Fig. 2. The shape of the a zigzag (10,0) nanotube under 15 V external electric field. It is viewed along the nanotube axis.

lations will be realized. Currently we are studying the possibility of similar structure relaxation caused by the electron-emission under a strong field, and the results will be published in a separate report.

Received January 2, 2003.

REFERENCES

1. Ijima, S. *Nature* **1991**, *354*, 56.
2. McEuen, P. L.; Fuhrer, M. S.; Pak, H. *IEEE Trans. On Nanotech*. **2002**, *1*, 78.
3. Dresselhaus, M. S.; Dresselhaus, G.; Eklund, P. C. *Science of Fullerences and Carbon Nanotubes*; Academic Press: San Diego, CA, 1996.
4. Dai, H.; Hafner, J. H.; Rinzler, A. G.; Colbert, D. T.; Smalley, R. E. *Nature* **1996**, *384*, 147.
5. Wong, S.; Joselevich, E.; Wooley, A.; Cheung, C.; Lieber, C. *Nature* **1998**, *394*, 52.
6. de Heer, W. A.; Chatelain, A.; Ugarte, D. *Science* **1995**, *270*, 1179.
7. Trans, S. T.; Verschueren, R. M., Dekker, C. *Nature* **1998**, *393*, 49.
8. Martel, R.; Schmidt, T.; Shea, H. R.; Hertel, T.; Avouris, Ph. *Appl. Phys. Lett.* **1998**, *73*, 2447.
9. Zhou, C.; Kong, J.; Dai, H. *Appl. Phys. Lett.* **1999**, *76*, 1597.
10. Campbell, S. A.; Kim, H.-S.; Gilmer, D. C.; He, B.; Ma, T.; Gladfelter, W. L. *IBM J. Res. Develop* **1999**, *43*, 383.
11. Derycke, V.; Martel, R.; Appenzeller, J.; Avouris, Ph. *Nano Letters* **2001**, *1*, 453.
12. Satio, R.; Dresselhaus, G.; Dresselhaus, M. S. *Physical Properties of Carbon Nanotubes*; Imperial College: London, 1998.
13. Lou, L.; Nordlander, P.; Smalley, R. E. *Phys. Rev. B*. **1995**, *52*, 1429.
14. Kim, C.; Kim, B.; Lee, S. M.; Jo, C.; Lee, Y. H. *Appl. Phys. Lett.* **2001**, *79*, 1187.
15. Rochefort, A.; Ventra, M. D.; Avouris, P. *Appl. Phys. Lett.* **2001**, *78*, 2521.
16. Payne, M. C.; Teter, M. P.; Allan, D. C.; Arias, D. C.; Johannopoulos, T. A.; Johannopoulos, J. *Rev. Mod. Phys.* **1992**, *64*, 1045.
17. *Cerius^2 User Guide*; Molecular Simulations: San Diego, CA, 1997.
18. Perdew, J. A.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B*. **1992**, *46*, 6671.
19. White, J. A.; Bird, D. M. *Phys. Rev. B*. **1994**, *50*, 4954.