

# Computational Nanotechnology: From Clusters to Devices

David Tománek

*Physics and Astronomy Department, Michigan State University, East Lansing, Michigan 48824-2320*

**Abstract.** This contribution describes recent applications of supercomputers to describing phenomena occurring on the nanometer scale, which evade direct experimental observation. Dependable ab initio calculations can determine, whether all-carbon nanostructures may become metallic or even magnetic. Computer simulations help us understand, how to design nanostructures with unusual properties, such as high thermal conductivity, thermal contraction, and even nanoscale bonding systems for NEMS devices.

**Keywords:** Nanotechnology, Supercomputing, Carbon Nanotubes, NEMS

**PACS:** 81.07.De, 61.48.+c, 68.70.+w, 81.05.Zx

## COMPUTATIONAL APPROACHES

The continuous reduction of device sizes, which is rapidly approaching the atomic level, calls for new approaches to design and test future building blocks of Nanotechnology. Computer modeling is an indispensable tool to interpret phenomena associated with the nanometer scale. Some of the most unexpected phenomena are displayed by carbon nanostructures.

Describing correctly the different types of bonding, which carbon is known to exhibit, poses a challenge. The Tersoff bond-order potential [1,2] has been used widely to obtain reliable equilibrium geometries and deformation energies of graphitic  $sp^2$  as well as diamond-like  $sp^3$  bonding. The continuum elasticity approach has shown unexpected accuracy when determining the strain energy in  $sp^2$  bonded single-wall carbon nanotubes and fullerenes [3]. Somewhat surprisingly, this approach, which ignores atomic positions in the graphite plate, has been able to reproduce accurately the formation energies of fullerenes and nanotubes down to diameters as small as 0.5 nm. Computationally more demanding, but still widely used, is a parameterized version of a total energy functional based on the Linear Combination of Atomic Orbitals (LCAO) electronic Hamiltonian [4]. Often called the tight-binding approach, this energy functional has proven especially useful in the description of transition states during structural changes, since it correctly represents the hybridization between s and p orbitals of carbon, which underlies the  $sp$ ,  $sp^2$  and  $sp^3$  bonding. This approach has gained wide popularity in molecular dynamics simulations, since it yields semianalytical expressions for interatomic forces, thus speeding up the simulation. In very large systems, where the diagonalization of a large Hamilton matrix is time limiting, the recursive reconstruction of the local density of states has proven very powerful, in particular due to its natural suitability for implementation on massively parallel supercomputers [5]. Assigning a processor to each atom, with information about the atomic arrangement in the close vicinity available, the local electronic density of states, the binding energy, as well as the force acting on that particular atom can be determined with a satisfactory precision.

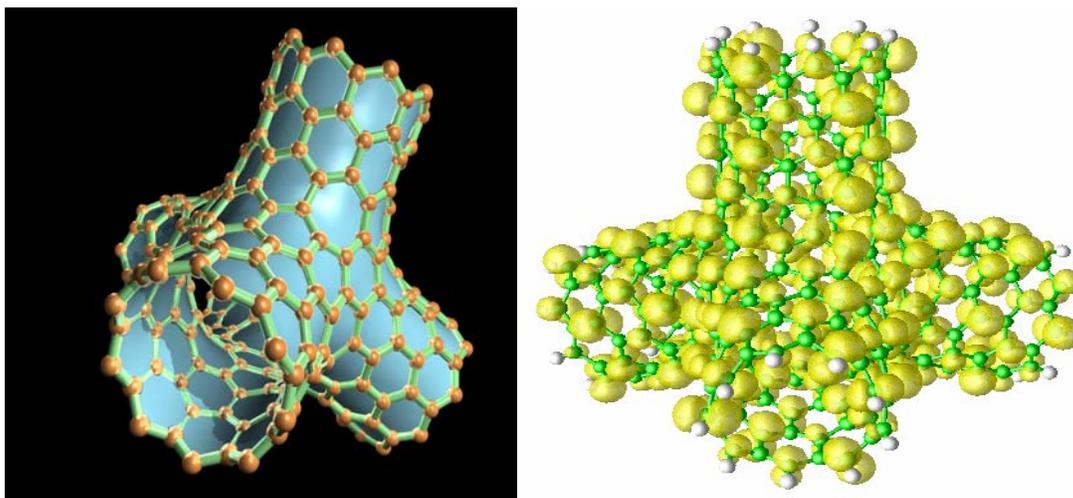
The method of choice to obtain accurate information about the total energy and ground state equilibrium geometry of nanostructures from first principles is the Density Functional Theory (DFT). Both the Local Density Approximation (LDA) [6,7] and the Generalized gradient Approximation (GGA)[8] have been used successfully to describe fullerenes, nanotubes, polymer chains, diamondoids, and other carbon allotropes. They are especially valuable in the description of hybrid structures and transition states, where a self-consistent determination of the charge distribution is essential.

Since many interesting carbon nanostructures exhibit graphitic  $sp^2$  bonding, their electronic states near the Fermi level are dominated by  $pp\pi$  hybridized atomic orbitals. The single-band Hückel Hamiltonian, which only considers  $pp\pi$  interactions, has been widely used to rationalize the electronic structure near the Fermi level in fullerenes and

nanotubes [9]. Sometimes incorrectly called the “tight-binding” Hamiltonian, in spite of its neglect of  $ss\sigma$ ,  $sp\sigma$ , and  $pp\sigma$  interactions, the Hückel Hamiltonian has been especially useful in discriminating between metallic and semiconducting nanotubes, an in relating the position of van Hove singularities in the electronic density of states to the tube diameter. Folding of the hexagonal Brillouin zone of the Bravais lattice of graphene monolayer, spanned by the basis vectors  $a_1$  and  $a_2$ , has been used to determine, whether the Fermi point  $K$  in the Brillouin zone corner is among the allowed wave-vectors, thus making a particular nanotube metallic [10]. Since every  $(n,m)$  nanotube can be characterized by the folding vector  $R=na_1+ma_2$ , which maps the graphene lattice onto itself, this simple consideration further suggests that only nanotubes with  $n-m$  divisible by 3 should be metallic. This powerful prediction has been confirmed experimentally.

## UNEXPECTED PHENOMENA IN NANOSTRUCTURES

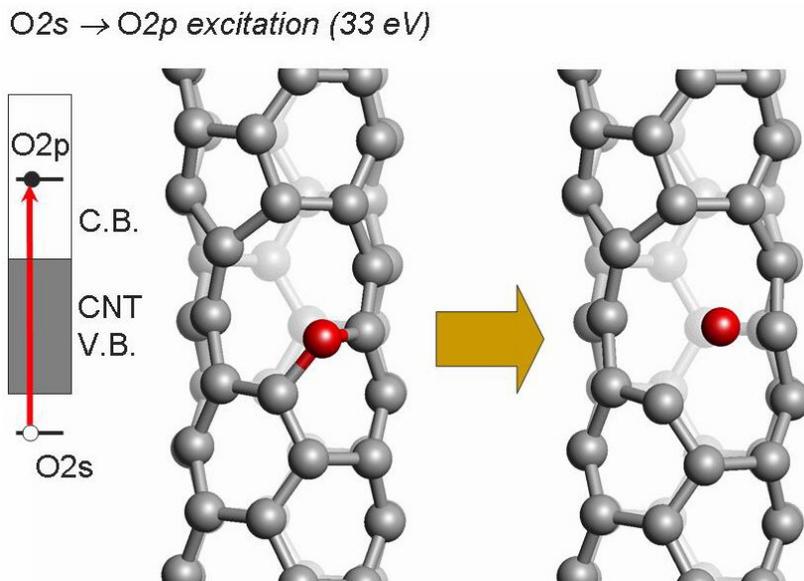
Due to the stability of the  $sp^2$  bond, carbon nanotubes are thermally and mechanically extremely stable and chemically inert. They contract rather than expand at high temperatures [11], and are the ultimate thermal conductors [12]. At the same time, nanotubes may be tuned into ballistic electron conductors or semiconductors.  $sp^2$  bonded nanostructures may change their shape globally by a sequence of Stone-Wales transformations [13]. Specific nanotube assemblies may even acquire a permanent magnetic moment [14,15] (see Figure 1).



**FIGURE 1.** (Color online) Structural model (left) and spatial distribution of majority-spin electrons responsible for magnetism (right) in an all-carbon nanostructures. (From Ref. 14, © American Physical Society.)

In nanostructures that form during a hierarchical self-assembly process, even defects may play a different, often helpful role. Efficient self-healing processes may convert less stable atomic assemblies into other, more perfect structures, thus answering an important concern in molecular electronics. Defects may even be used in nano-scale engineering to form complex systems such as carbon foam or nanotube peapods [16].

Recent computer simulations of defective nanotubes indicate an amazing self-healing ability of these nanostructures at elevated temperatures or in the electronically excited state [17]. To a large degree, nanostructures owe this unexpected behavior to their larger structural flexibility in comparison to large systems. Electronic excitations also last for a significant fraction of the atomic vibration period in nanostructures, thus capable of breaking or forming atomic bonds. This particular behavior is expected to prove very useful, when trying to establish selective purification techniques for nanostructures, including photoinduced deoxidation of defective nanotubes [18] (see Figure 2).

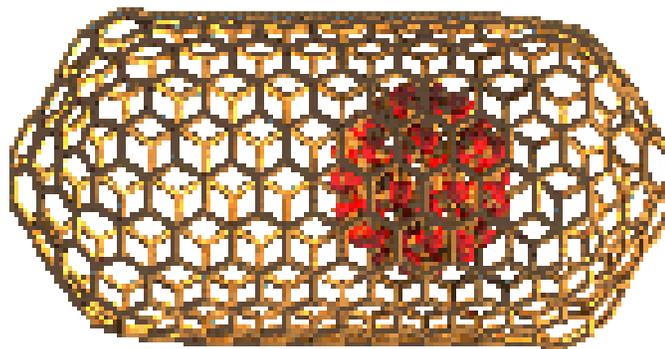


**FIGURE 2.** Photo-induced de-oxidation of a defective carbon nanotube. (From Ref. 18, © American Physical Society.)

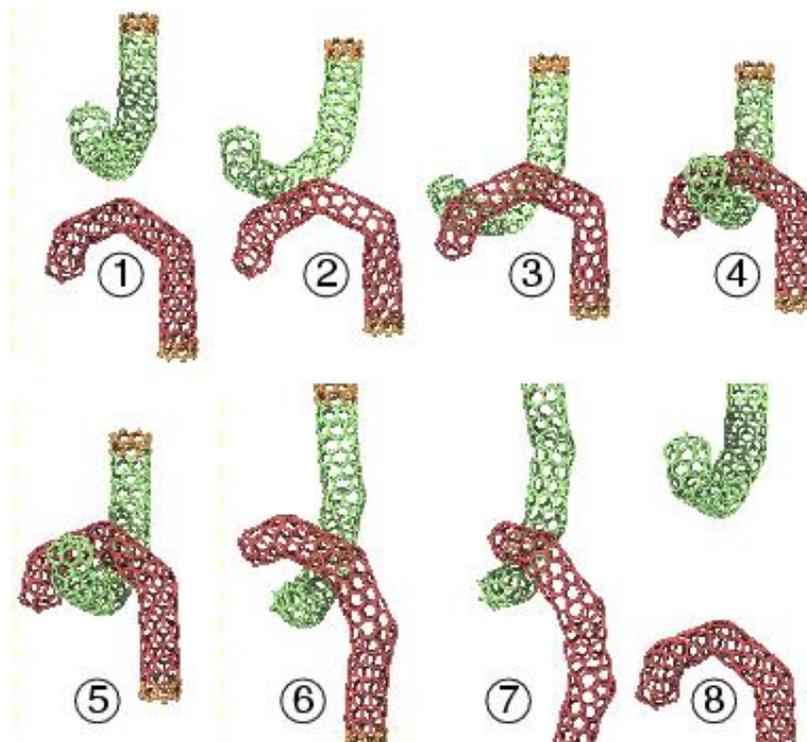
## DEVICE APPLICATIONS OF NANOSTRUCTURES

Unusual behavior is expected of devices based on nanotubes, including nonvolatile computer memory elements (see Figure 3), consisting of metallofullerenes encapsulated in nanotubes [19], or pairs of nanotube hooks, capable of connecting nanostructured surfaces by a counterpart of the Velcro bond [20] (see Figure 4).

Hierarchically self-assembled nanostructures consisting of polyacetylene [21] or polymerized diamondoids [22], enclosed in carbon nanotubes, may exhibit unusual transport properties and find use as functional building blocks of complex Nano-Electromechanical Systems (NEMS).



**FIGURE 3.** (Color online) A fullerene molecule inside a nanotube as a prototype non-volatile memory element capable of storing one bit information [U.S. Patent 6,473,351]. (From Ref. 19, © American Physical Society.)



**FIGURE 4.** (Color online) Snap shots of engaging (1-4) and disengaging (5-8) nanotube-based “nanovelcro” hooks. (From Ref. 20, © American Physical Society.)

## ACKNOWLEDGMENTS

I would like to acknowledge especially my close collaborators Savas Berber, Young-Kyun Kwon, Gregory C. McIntosh, Yoshiyuki Miyamoto, Noejung Park, and Mina Yoon. Partial financial support for this work has been provided by NSF-NIRT grant DMR-0103587 and NSF NSEC Grant Number 425826. Resource allocation on the “Earth Simulator” supercomputer has been arranged by the RIST Computational Nanotechnology Program (Japan).

## REFERENCES

1. J. Tersoff, *Physical Review B* **37**, 6991 (1988).
2. J. Tersoff, *Physical Review Letters* **61**, 2879 (1988).
3. D. Tománek, W. Zhong, and E. Krastev, *Phys. Rev. B* **48**, 15461 (1993).
4. D. Tománek and Michael A. Schluter, *Phys. Rev. Lett.* **67**, 2331 (1991).
5. W. Zhong, D. Tománek and George F. Bertsch, *Solid State Commun.* **86**, 607 (1993).
6. P. Hohenberg and W. Kohn, *Physical Review* **136**, B864 (1964).
7. W. Kohn and L. Sham, *Physical Review* **140**, A1133 (1965).
8. J. P. Perdew, J. Chevary, S. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, *Phys. Rev. B* **46**, 66716687 (1992).
9. R. Saito, M. Fujita, G. Dresselhaus, and M. Dresselhaus, *Applied Physics Letters* **60**, 2204 (1992).
10. N. Hamada, S. Sawada, and A. Oshiyama, *Physical Review Letters* **68**, 1579 (1992).
11. Young-Kyun Kwon, Savas Berber, and David Tománek, *Phys. Rev. Lett.* **92**, 015901 (2004).
12. Savas Berber, Young-Kyun Kwon and David Tománek, *Phys. Rev. Lett.* **84**, 4613 (2000).
13. Mina Yoon, Seungwu Han, Gunn Kim, Sangbong Lee, Savas Berber, Eiji Osawa, Jisoon Ihm, Mauricio Terrones, Florian Banhart, Jean-Christophe Charlier, Nicole Grobert, Humberto Terrones, Pulickel M. Ajayan, David Tománek, *Phys. Rev. Lett.* **92**, 075504 (2004).
14. Noejung Park, Mina Yoon, Savas Berber, Jisoon Ihm, Eiji Osawa, and David Tománek, *Phys. Rev. Lett.* **91**, 237204 (2003).

15. Jin Choi, Yong-Hyun Kim, K. J. Chang, and David Tománek, Phys. Rev. B 67, 125421 (2003).
16. Savas Berber, Young-Kyun Kwon, and David Tománek, Phys. Rev. Lett. 88, 185502 (2002).
17. Yoshiyuki Miyamoto, Savas Berber, Mina Yoon, Angel Rubio, David Tománek, Chem. Phys. Lett. 392, 209 (2004).
18. Yoshiyuki Miyamoto, Noboru Jinbo, Hisashi Nakamura, Angel Rubio, and David Tománek, Phys. Rev. B 70, 233408 (2004).
19. Young-Kyun Kwon, David Tománek, and Sumio Iijima, Phys. Rev. Lett. 82, 1470 (1999).
20. Savas Berber, Young-Kyun Kwon, and David Tománek, Phys. Rev. Lett. 91, 165503 (2003).
21. G.C. McIntosh, D. Tománek, and Y.W. Park, Phys. Rev. B 67, 125419 (2003).
22. G. C. McIntosh, M. Yoon, S. Berber, N. Park, E. Osawa, and D. Tománek, Phys. Rev. B 70, 045401 (2004).