Electronic structure of short and long carbon nanotubes from first principles

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First-principles calculations within the density-functional theory are carried out on carbon nanotubes with finite as well as infinite lengths. Quantum confinement effects, different from those in silicon clusters and carbon nanoparticles are predicted. It is shown that the electronic density of states of finite-length tubes resembles that of infinitely long tubes for tube lengths of only a few nanometers. A plot of the square of the wave function along the length of the tube shows periodic variation with a period of 0.4 nm, in agreement with recent measurements of I-V curves in short armchair tubes. [S0163-1829(99)02515-1]

Ever since their discovery in 1991 by Iijima,[1] carbon nanotubes have been the subject of intensive experimental and theoretical efforts. It has been predicted that some carbon nanotubes are metallic while others are semiconducting, depending on their diameter and chirality.[2–4] Both of these factors determine the symmetry operations that describe the structure of carbon nanotubes, and consequently determine their electronic and lattice properties.[5–6] Experiments probing the electronic structure of carbon nanotubes have been carried out over the last few years[7–11] but only very recently has it become possible to study experimentally the correlation between nanotube diameter and chirality on the one hand, and the electronic properties on the other.[12,13] Scanning tunneling microscopy (STM) and spectroscopy were used to measure the electronic structure of nanotubes, in terms of the density of states, and their physical structure, in terms of the nanotube diameter and chiral angle. Armchair, zigzag, and chiral tubes of various diameters were used in these studies. The measured density of states shows a series of peaks corresponding to the onset of subsequent energy bands. For semiconducting nanotubes a relatively small gap is observed, whereas larger gaps, which increase with decreasing tube diameter, were observed for metallic nanotubes.

Understanding the dependence of the electronic structure of nanotubes on their lengths, diameters, and helicities is of vital importance for their possible use in nanoelectronics applications,[14,15] where carbon nanotubes could be used as junctions,[16] bends,[17] or the building blocks of transistors and electron emitters of nanometer dimensions.[14] Indeed, a field-effect transistor consisting of one semiconducting single-walled (SW) carbon nanotube connected to two metal electrodes has been recently fabricated and operated at room temperature;[18] similar behavior was obtained earlier for metallic SW carbon nanotubes operated at extremely low temperature.[19]

Most recently, it has become possible to cut nanotubes and control their length by applying voltage pulses to the tip of an atomic force microscope above a nanotube.[20–22] The resulting ''fullerene capsules'' are molecules of carbon with a number of atoms ranging from several hundreds to several thousands. STM has been used to map the electronic wave functions along the length of a short armchair (10,10) carbon nanotube 30-nm long.[20] The steplike behavior of the current-voltage curve, in contrast to the linear dependence displayed in infinitely long nanotubes,[12–13] demonstrates the quantum confinement in this system. At a low-bias voltage the measured current, as a function of position along the tube axis, shows periodic variation with a period of about 0.37 nm.[20] Tight-binding calculations of the energy gap as a function of tubule length, using nearest neighbor interactions, has been recently reported in the literature.[23]

In this paper, we report first-principle calculations of the density of states (DOS) for tubes of finite as well as infinite lengths and of various diameters and helicities. We consider the armchair tubes (5,5) and (10,10) and the chiral tube (12,8). Tubes of finite lengths are capped by hydrogen rings on both ends in order to avoid the problem of dangling bonds. For these ''capsules'' the calculation of the electronic energy levels is carried out using an *ab initio* density-functional method based on a three-dimensional numerical integration[24] of the Kohn-Sham one-particle equations using a local-density approximation (LDA) potential.[25] A double valence plus a single polarization basis, which provides an accuracy comparable to the 6-311 G** Gaussian basis set,[26] has been used for both C and H atoms.

The electronic energy bands of the infinitely long nanotubes are calculated within a density-functional method, which calculates the total energy and the electronic structure within a one-dimensional band-structure approach.[27,28] Since the group generated by a helical symmetry operation is isomorphic with the one-dimensional translation group, it follows that a generalization of Bloch's theorem allows us to define a unit cell with N atoms such that starting with these N atoms the whole lattice of nuclear coordinates can be generated by the repeated application of the helical symmetry.

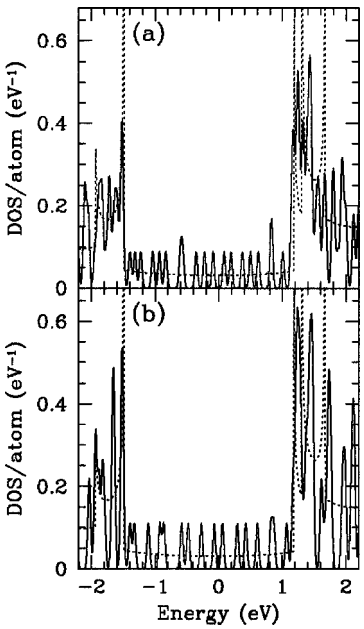

FIG. 1. Density of states (DOS) for the (5,5) carbon nanotubes. The solid lines represent the DOS for short nanotubes whereas the dotted lines correspond to infinitely long tubes. The short tube in (a) has 42 C rings for a total of 420 C atoms and is 5.25-nm long while that in (b) has 34 C rings and is 4.25-nm long. In plotting the DOS for the short tubes each discrete energy level is replaced by a gaussian with full width at half maximum (FWHM) given by 0.05 eV.

For the (5,5), (10,10), and (12,8) tubules considered in this study, N is given, respectively by 10, 20, and 8.

The results of these calculations are shown in Figs. 1–3, where the DOS is plotted as a function of the energy. Figure 1 shows the DOS for the (5,5) metallic tubes. A wide energy gap separates two sharp peaks above and below the Fermi level, which for a short tube is filled with uniformly distributed discrete states that tend to a continuum of constant value as the tube length increases. Figure 2 shows another metallic tube, (10,10), where the energy gap with ''constant'' DOS is narrowed due to increased diameter. The DOS in Fig. 2(b) is for a tube only 1.6-nm long, and shows accordingly more molecular character. For the (12,8) semiconducting tubes, the DOS in Fig. 3 shows a finite band gap.

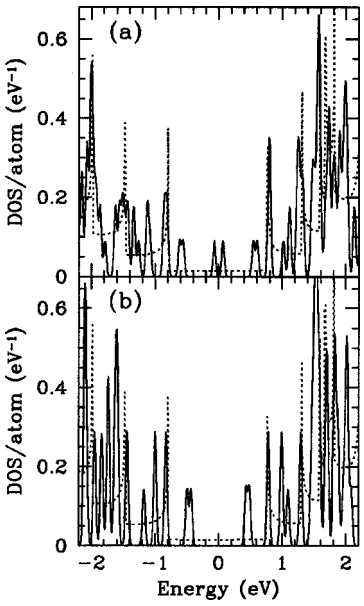

FIG. 2. Density of states for (10,10) carbon nanotubes. The solid lines refer to tubules of finite length whereas the dotted lines refer to infinitely long ones. The short tube in (a) has 21 C rings (420 C atoms) and is 2.6-nm long, whereas that in (b) has 13 C rings (260 C atoms) and is 1.6-nm long. Discrete energy levels are modeled with a gaussian with 0.05 eV FWHM.

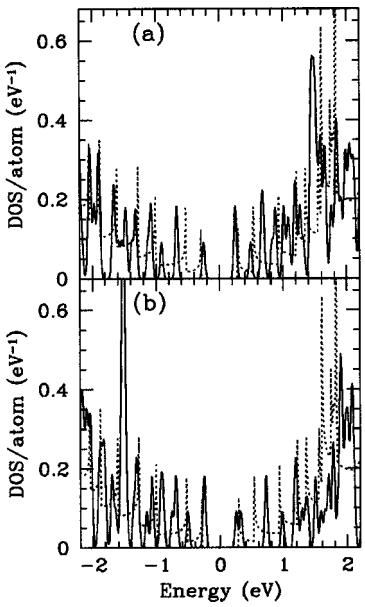

FIG. 3. Density of states for (12,8) chiral semiconducting carbon nanotubes. Solid lines refer to tubes of finite length whereas dotted lines refer to infinitely long tubes. The short tube in (a) has 412 C atoms and is 2.35-nm long whereas that in (b) has 460 C atoms and a length of 2.6 nm. Discrete energy levels are modeled with a gaussian with 0.05 eV FWHM.

For both metallic and semiconducting cases, these figures show a rather striking resemblance of the DOS for short tubes to that for long tubes. Particularly, the position of the sharp peaks predicted agrees well with experiment.[12,13] This confirms that satisfactory results can be obtained within the LDA framework, for which an all-electron, *ab initio* treatment is feasible for systems containing a few hundred atoms. Using a generalized gradient approximation to replace the LDA exchange-correlation potentials does not result in any significant changes in the DOS features shown in Figs. 1–3. For simplicity, we did not consider quasiparticle gaps in this calculation, though it provides a more accurate estimate for the lowest excitation energy, which is relevant to transport properties.

Also, for tubes considered here which contain up to 460 C atoms, no significant dependence on length is observed for the major features in the DOS (the position of the sharp peaks for the metallic case and the band gap for the semiconducting case), as a result of quantum confinement. This is in contrast to the case of silicon for which recent calculations[29] predict, using LDA formalism, that the band gap will be about a factor of two larger as the diameter of the silicon quantum dot decreases from infinity to near 1 nm, and the case of carbon nanoparticles for which experiments show a significant dependence of the electronic properties on cluster size.[30]

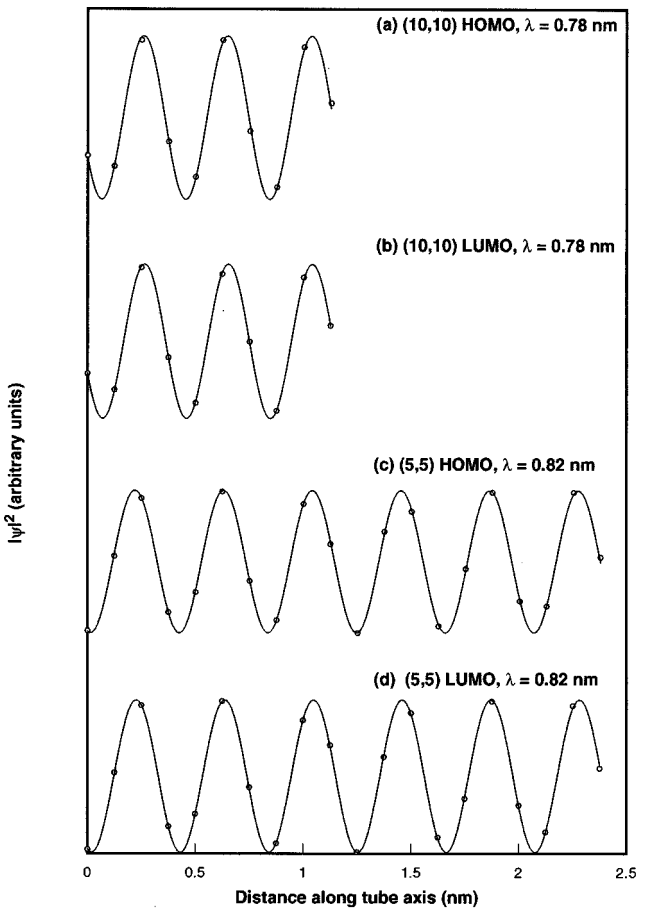

FIG. 4. Square of the wavefunction for short armchair tubes plotted as a function of the distance along the tube axis starting from a region near the center and moving towards the tube edge. Results for both the HOMO and LUMO are shown. The open circles are the results of the calculations in this work; they are fitted by the sine square function shown in the narrative.

We have also calculated the square of the wave function for the highest occupied and lowest unoccupied molecular orbital (HOMO and LUMO) for the (5,5) and (10,10) metallic tubes. The results are shown in Fig. 4 where $|\Psi|^2$ is plotted as a function of the distance along the tube axis, starting near the center of the ''capsule'' and moving towards its edge. The evaluation of $|\Psi|^2$ is carried out at discrete values along the z axis (the tube axis direction) by adding the contributions of all atoms having the same value of z; for the (5,5) nanotube, for example, the ten atoms belonging to each ring have the same value of z. By fitting these $|\Psi|^2$ values to the function $A\sin^2[(2\pi x/\lambda)+\phi]+B$ we obtain values for λ given by 0.82 and 0.78 nm for the (5,5) and (10,10) capsules, respectively. These agree fairly well with the experimentally reported values for λ ranging from 0.66 to 0.76 nm as deduced from measurements of dI/dV at low bias for short (10,10) tubules.[20]

A more accurate treatment of unoccupied energy levels and bands requires a more sophisticated formalism, like the gradient weighted (GW) approximation,[31] a method difficult to apply to the systems considered here because of the immense computational resources that are needed. The conclusions arrived at in this work, however, are expected to continue to hold. In comparing the DOS for short and long tubes, the calculations for both systems are carried out within LDA, and thus both systems are subject to the same kind of approximations. Furthermore, the energy gaps of semiconducting nanotubes, and the position of the sharp peaks in the DOS for metallic and semiconducting tubes, are in very good agreement with experimental results, as well as with theoretical results derived from the graphene sheet model.[32] In this latter model, unconnected with LDA, the only errors involved have to do with the neglect of curvature effects, which are important only for tubes with very small diameters. The periodic variations in $|\Psi|^2$, for states in the vicinity of the Fermi level, are a consequence of the charge-density wave state in long nanotubes, and it is thus a ground state property, which is well described by LDA. Our results for short tubes imply that this property persists to very short tube lengths.

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