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Atomic restructuring and localized electron states in a bent carbon nanotube: A first-principles study

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We apply first-principles calculations to study structural and electronic properties of a semiconductor carbon nanotube bent to a large angle. The geometry optimization results in fourfold carbon rings at the bend region. These fourfold rings, seldomly seen in carbon structures, result from the collapse of carbon hexagons at the most stressed region of the bend. Part of the atoms at the fourfold rings are also fourfold coordinated, which indicates a strong sp^3 character. Localized electron states are found at the bend region, making the bent tube behave as a quantum dot. This bending-induced quantum dot can be charged with one electron or one hole at most.

Since carbon nanotubes were first synthesized in 1991,[1] they have attracted an increasing interest due to their electronic and mechanical properties. Concerning the mechanical properties, theoretical and experimental results[2–4] predict a high Young modulus for carbon nanotubes, comparable to or greater than that of diamond. In contrast, carbon nanotubes are very flexible: high-resolution electron microscope experiments, together with empirical-potential modeling, have shown that carbon nanotubes are extremely flexible, and can be bent at large angles without fractures.[5] Other experimental results also show the bending of nanotubes, either as a result of their embedment within a polymeric film[6] or as a result of lateral stresses applied by the tip of an atomic force microscope.[7] So far, theoretical investigations on structural properties of bent carbon nanotubes have been limited to empirical-potential modeling. These investigations[5,8,9] show the existence of a critical angle[10] beyond which a kink is formed at the central region of the bend.

In the present work we apply first-principles calculations to the study of structural and electronic properties of a semiconductor carbon nanotube bent to a large angle. In contrast to previous empirical potential results, we find the formation of fourfold carbon rings at the bend region. These fourfold rings, unusual for carbon structures, result from the collapse of carbon hexagons at the most stressed region of the bend. Part of the atoms at the fourfold rings are also fourfold coordinated, which indicates a strong sp^3 character. Concerning the electronic properties, we find that they are strongly affected by the bending of the tube. Indeed, discrete states predominantly localized at the bend region are found in the energy gap range, making the bent tube behave as a quantum dot.[11] We also find that the bending-induced quantum dot can be charged with one electron or one hole at most, and can only exist in three charge states.

Our calculations were performed with the SIESTA program[12–14] using the density-functional theory,[15] within the generalized gradient approximation for exchange-correlation,[16] and norm-conserving pseudopotentials.[17,18] This methodology was previously applied to the study of structural and electronic properties of nanotubes and fullerenes.[19,20] The basis set is a linear combination of pseudoatomic orbitals of finite range.[21,22] All the geometries were optimized, aiming at a convergence of the atomic positions (shown in Fig. 2) within 0.09 Å and a convergence of the density of states (shown in Fig. 4) within 0.05 eV. With the methodology described, the calculated geometries of the C_{60} molecule and of the bulk graphite agree with experimental results[23] within 5%.

In our calculations, we consider a zigzag (10,0) nanotube 8 Å in diameter, a semiconductor in the limit of infinite length, bent to a large angle. The choice of this tube is justified by the fact that a bent single-wall nanotube (SWNT) of this diameter was already observed by Iijima *et al.*[5] The bent angle used (92°) is also consistent with the experimental observations. We simulate the bent nanotube by a zigzag-shaped large unit cell of 400 carbon atoms with periodic boundary conditions. We antecipated that, as a result of the geometry relaxation, the nanotube would flatten near the bent region. Based on this consideration, we adopted the initial geometry shown in Fig. 1 as the starting point of the calculation.[24]

The final result after the geometry optimization is shown in Fig 2. The cross section of the tube is increasingly flattened as one approaches the region of the largest curvature. At this point, a kink is formed. The kink is very sharp and localized within a length of about 4 Å.[25,26] This is consistent with the experimental results of Ref. 10. In contrast, force-field-based optimizations predict a smoother and less localized kink region.[9] The degree of flatness at the kink predicted by our calculations is such that it acquires the appearance of a bilayerlike structure with an interlayer distance of 3.2 Å. This structural change, as we shall show, strongly affects the local electronic structure of the tube.

Our first-principles geometry optimization also shows the existence of carbon atoms arranged in fourfold rings at the most strained region of the kink, as seen in Fig. 2. Unlike fivefold and sevenfold rings,[27–31] fourfold rings are seldomly seen in carbon structures, and do not occur in carbon fullerenes due to their high energy cost,[32] in contrast to boron nitride fullerenes, where fourfold rings are expected to occur.[32,20] The fourfold rings of the bent nanotube originate from the collapse of graphitelike hexagonal rings. Some of the carbon atoms at the fourfold rings are also fourfold coordinated, which indicates the existence of a strong sp^3 char-

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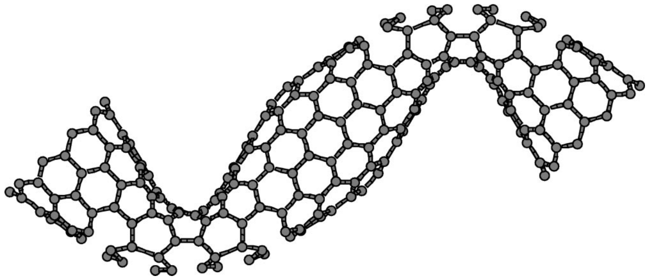

FIG. 1. Structure of the unit cell used as the starting point of the calculation. It consists of a zigzag (10,0) carbon nanotube 8 Å in diameter, bent to an angle of 92°. The unit cell is composed of 400 atoms, and periodic boundary conditions are used in the calculations. The cross section of the bent nanotube is increasingly oval in the direction of the top of the bend.

acter. The atomic neighborhood where the fourfold rings are present is emphasized in Fig. 3. The geometry shown in this figure resembles the faces of the C_8H_8 cubane, an unusual molecule in which the carbon atoms are arranged in a simple cubic structure.[33,34]

The strong deformations of the bent tube shown in Fig. 2 are found to significantly affect the electronic structure near the bend region. To investigate that, we calculated the local density of states (LDOS) in distinct parts of the bent tube. We consider two regions, indicated by labels in Fig. 2: region 1, bulklike, is the farthest from the kink, and region 2 is at the kink. The LDOS is averaged over 60 atoms present in each region. The results are shown in Fig. 4. The reference energy is the Fermi level of the deformed tube, and the edges of the valence and conduction bands of the undeformed tube are indicated as dashed lines. The figure shows the existence of gap states induced by the bending. The local density of these gap states increases progressively in the direction of the kink. In addition, resonant peaks of increasing amplitude appear in the conduction and valence bands of the tube, distant about 0.7 eV from the Fermi level. Similar resonances have been observed in extended Hückel calculations[8,9] of bent metallic nanotubes.

Figure 4 clearly shows that the gap states are predominantly localized at the kink (region 2). The localization of the gap states is consistent with the fact that the bend region can be considered as a localized defect of the infinite, undeformed semiconductor tube. Our results also show that the one-electron eigenvalues are nearly degenerate at the Fermi level. The energy difference between the lowest unoccupied and the highest occupied molecular orbitals [the highest-occupied–lowest-unoccupied molecular-orbital (HOMO-LUMO) gap] is found to be 0.04 eV. This is to be compared to the original value of 0.9 eV for the infinite, undeformed

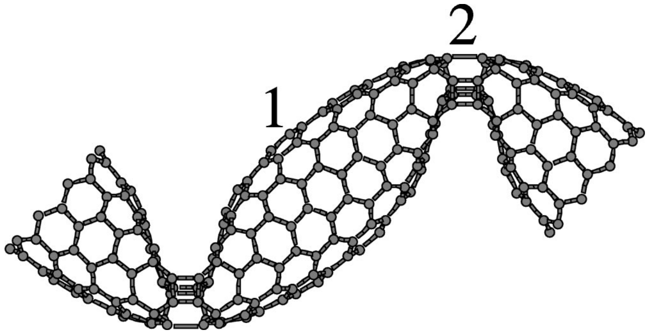

FIG. 2. Structure of the bent nanotube after the geometry optimization. A sharp and localized kink is formed at the region where the curvature is larger. Fourfold-coordinate carbon atoms can be viewed at the kink. The labels refer to the regions in which the local density of states is calculated.

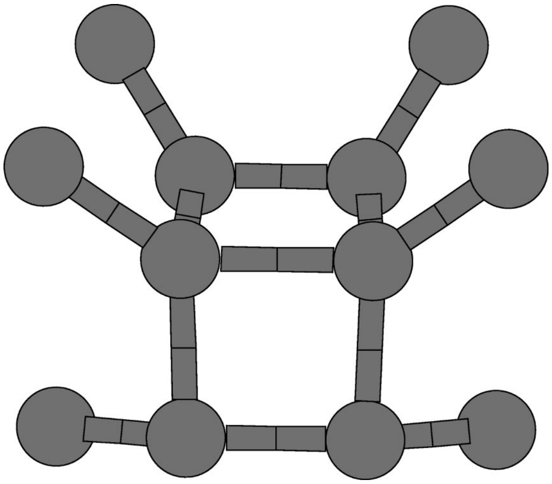

FIG. 3. Zoom of the four-membered rings at the kink region, showing the fourfold-coordinate carbon atoms. The angle between the two adjacent four-memebered rings is 95°.

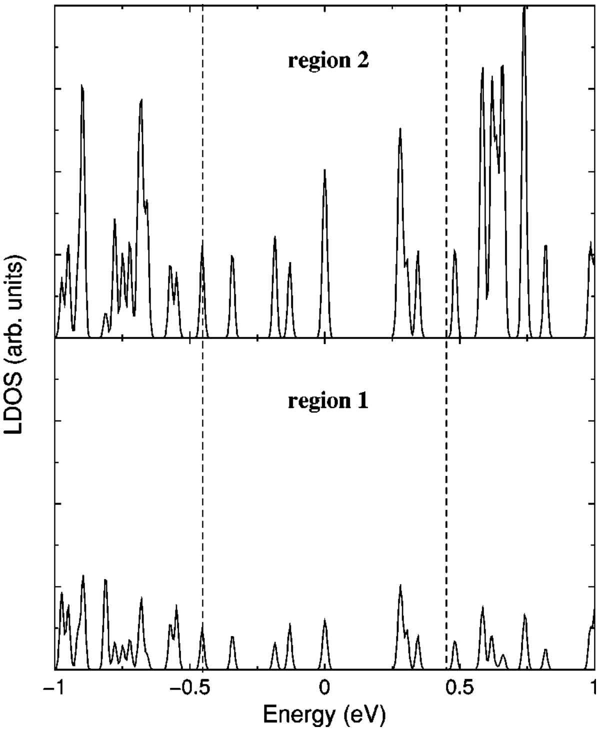

FIG. 4. Local density of states (LDOS) for the two distinct regions of the bent nanotube: region 1, bulklike, is the farthest from the kink; and region 2 corresponds to the kink (see Fig. 2). The dashed lines indicate the edges of the valence and conduction bands of the undeformed nanotube. The gap states are predominantly localized at the kink region. The energy reference is the Fermi level of the bent nanotube, and the LDOS is averaged over the 60 atoms present in each region.

tube. To investigate the effect of the periodic boundary conditions on the above results, calculations were also performed for a structure composed of a single kink formed by half of the periodic structure shown in Fig. 2. This single-kink structure is composed of 200 carbon atoms with 20 hydrogen atoms saturating the dangling bonds at the tube ends. The LDOS calculated for this kink is very similar to the one shown in region 2 of Fig. 4. Also, the HOMO-LUMO difference in this structure is 0.02 eV, showing that the small gap at the Fermi level observed in the periodic structure is not caused by interactions between the two bent regions.

To further investigate the electronic structure of the bent tube, we performed a charge-density analysis of the (HOMO and LUMO) wave functions, ψ_H and ψ_L, by calculating the Mulliken charges q_i^H and q_i^L at all carbon sites i. The Mulliken charge of a wave function ψ at site i is defined as $q_i = \langle \psi | \Sigma_\alpha (|\phi_i^\alpha\rangle\langle\phi_i^\alpha| + \frac{1}{2}\Sigma_{j\neq i} |\phi_i^\alpha\rangle\langle\phi_j^\alpha|) |\psi\rangle$, where ϕ_i^α is the αth basis function at site i. With this definition, q_i can be associated with the projected norm of ψ at site i. Our results show that q_i^H and q_i^L are smaller than 0.06 at any site. The sites with the largest q_i^H and q_i^L are carbon atoms at the central part of the bend region, distant from the carbon atoms at the fourfold rings. In this way, ψ_H and ψ_L are not localized at the fourfold rings, but rather at the outer side and (to a less extent) at the inner side of the bend. If we use the probability densities of ψ_H and ψ_L as measures of the chemical reactivity, the above results would indicate that the outer part of the bend would be the most susceptible to chemical attack. This suggests that bending a carbon nanotube might stimulate chemical reactions at specific sites of the tube wall, providing selective sites for attaching a molecular radical or opening small holes, for instance. This is consistent with the prediction by Dekker[35] that nanotube chemistry will be particularly interesting at tube ends and also near buckles.

The density of states (DOS) shown in Fig. 4 is constructed with the one-electron eigenvalues of the neutral system. However, if measurements on the bent tube are performed with a scanning tunneling microscope (STM) or a similar technique, electrons will be transferred from or onto the tube. If the localized electronic states in the bend region are weakly coupled to the surface states of the substrate, the STM will not directly probe the DOS of Fig. 4. Instead, the STM will probe the transition energies between different charge states of the bent tube. We calculated these transition energies as follows:[36,37] First, we calculated the formation energies $E(q)$ of the bent tube in several charge states $q(q = +2, +1, 0, -1, -2)$ as functions of the electronic chemical potential μ, $E(q) = E_t(q) + q\mu$. In the previous equation, $E_t(q)$ is the total energy of the bent tube with net charge q, calculated with a hydrogen-terminated finite-size cluster of 200 carbon atoms and 20 hydrogen atoms. The geometry of the carbon atoms corresponds to half of the unit cell of Fig. 2 (a single bend). The actual charge state q for a given value of μ is the one that gives the smallest $E(q)$. The transition energies correspond to the values of μ where q changes. With the procedure described above, we obtain the $(+/0)$ and $(0/-)$ transitions located at 0.26 and 0.54 eV, respectively, above the top of the valence band. These are the only transitions in the band gap. That is, the bent tube quantum dot is only found in the charge states $+1$, 0, and -1. It is worth mentioning, regarding to the above results, that quantum dots with charge state transitions separated in energy by tenths of an eV are promising building blocks for room-temperature nanoelectronics.

In conclusion, our first-principles calculations show that a bent carbon nanotube presents a considerable restructuring of the carbon bonds at the bend region. The restructuring is clearly manifested by the formation of fourfold carbon rings. These fourfold rings, unusual for carbon structures, result from the collapse of carbon hexagons at the highest stressed region of the bend. Part of the atoms at the fourfold rings are also fourfold coordinated, which indicates the existence of a strong sp^3 character. Concerning the electronic properties, we find that they are strongly affected by the bending of the tube. Indeed, discrete and localized states are found in the bend region, making a semiconductor bent tube behave like a quantum dot. We also find that this bending-induced quantum dot can be charged with one electron or one hole at most, and thus occuring only in three charge states. The corresponding charge-state transitions are separated in energy by 0.28 eV, and therefore the quantum dot would have a well-defined charge state at room temperature. This means that it could be considered, in principle, as a building block for room-temperature nanoelectronic devices.

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[25] In general, the shape of the kink will be a function of the diameter and chirality of the nanotube. For instance, for single-wall nanotubes of very large diameters, flattening is a spontaneous distortion (Ref. 26), and kinks should not even exist.

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