

Electronic properties of carbon nanotubes with polygonized cross sections

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The electronic properties of carbon nanotubes having polygonized cross sections instead of purely circular ones, such as recently observed using transmission electron microscopy, are investigated with plane-wave *ab initio* pseudopotential local-density-functional calculations and simple *tight-binding* models. Strong σ^* - π^* hybridization effects occur in zigzag nanotubes due to the high curvature located near the edges of the polygonal cross-section prism. These effects, combined with a lowering of symmetry, dramatically affect the electronic properties of the nanotubes. It is found that modified low-lying conduction-band states are introduced either into the bandgap of insulating nanotubes, or below the degenerate states that form the top of the valence band of metallic nanotubes, leading the corresponding nanostructures to be metals, semimetals, or at least very-small-gap semiconductors. The degree of the polygon representing the cross section of the tube, and the sharpness of the edge angles, are found to be major factors in the hybridization effect, and consequently govern the electronic behavior at the Fermi level. [S0163-1829(96)50436-4]

Recently, experimental observations have shown that carbon nanotubes might not be as perfect as they were once thought to be: pure cylindrical rolled-up graphene sheets.^{1,2} In particular, electron microscope images of some carbon nanotubes revealed the presence of nonsymmetric lattice fringes, suggesting that the tube cross section could be polygonal and not always circular, as previously believed.³ Holographic transmission-electron-microscopy observations, where three-dimensional information is obtained, in contrast to that with traditional intensity images, also prove the presence of a clear faceting in some of these nanometer carbon systems.⁴ In these polygonized nanotubes, the section is composed of straight portions joined by narrow regions of high curvature. Due to the ability of the carbon to rehybridize between pure sp^2 (graphite) and pure sp^3 (diamond), a graphene sheet with the assumed out-of-plane bends along the edges of the polygonal prism must lose some of its sp^2 character there and gain some sp^3 hybridization, thereby reaching a $sp^{2+\alpha}$ character where α is a factor dependent on the degree of curvature of the bend. The polygonized edges can then be considered as defected lines of rehybridization in the sp^2 network, with strong sp^3 character in the fold. Nanotubes mechanically deformed also appear to be rippled indicating the presence of ridges with analogous sp^3 character.⁵ Irregularities in these localized variations of the carbon bonding are undoubtedly responsible for significant effects on the electronic properties of nanotubes which the present study aims at exploring.

The electronic structure of a perfect nanotube is known to be either metallic or semiconducting, depending on its diameter and chirality,⁶⁻⁸ which can uniquely be determined by the chiral vector (n,m) , where n and m are integers.⁸ A

general rule can be derived: metallic or semiconducting nanotubes are obtained whether or not $n-m$ is a multiple of 3, neglecting the opening of a small gap due to the curvature.⁹ In this work, we investigate the perturbation of the electronic properties of carbon nanotubes brought about by a "polygonization" of their cross section. The electronic properties of both polygonized armchair (n,n) and zigzag nanotubes $(n,0)$ are examined in the framework of *ab initio* and *tight-binding* calculations. Different degrees of polygon (3: triangle, 4: square, 5: pentagon, 6: hexagon) are considered, and the results obtained indicate that the gap of zigzag nanotubes polygonized cross sections is significantly affected by σ^* - π^* states hybridization effects, which occur locally at the polygonized edges. This σ^* - π^* hybridization, which has already been shown to impose dramatic changes in the electronic properties of very-small-radius zigzag nanotubes,¹⁰ is only possible in the *zigzag* geometry where the C-C bond is parallel to the axis of the tube. In this connection, the electronic behavior of *armchair* nanotubes is not so strongly altered by the "polygonization" as discussed below.

The fact that a semiconducting nanotube can be driven to a metallic or semimetallic state by hybridization defects might underline that most carbon nanotubes synthesized using an arc discharge between two carbon rods, and where high curvature defects are often observed, can then be considered as conducting nanowires. In addition, when optimal conditions for bulk growth mechanism are satisfied,¹¹ nanotubes appear to grow most often in microbundles. Each nanotube is then neatly packed and aligned with four, five or six (in a perfect hexagonal closed packing arrangement) nearest neighbors.¹² When the diameter is large enough, the

tubes flatten against each other under the van der Waals attraction, forming different faceted cross sections for the constituents of the bundle. In a hypothetical carbon-nanotube crystal, this flattening process would be the consequence of the subtle competition between elastic deformation energy and van der Waals interaction.¹³ Similar distortions have also been observed for pairs of nanotubes.¹⁴ How this atomic relaxation modifies the electronic properties of the nanotubes in a solid-state packing can be appreciated by considering a single, deformed tube as a brick of the edifice.

We have carried out both *ab initio* pseudopotential local-density-approximation (LDA) calculations¹⁵ and Slater-Koster *tight-binding* (TB) calculations¹⁶ to investigate the electronic properties relative to different armchair (n,n) and zigzag $(n,0)$ nanotubes with polygonized cross sections, where ℓ is the degree of the cross-section polygon. These systems were selected because their electronic properties are known to differ radically. No calculations were performed for polygonized helical nanotube (n,m) (where $n \neq m$), as such a topology is an intermediate case between the two ones considered here. The LDA electronic structure calculations were performed using a plane-wave basis set (± 20.000 PW). The atomic potentials plus core electrons of carbon have been replaced by conventional *ab initio* pseudopotential for carbon.¹⁷ The energy cutoff for the electronic wave functions was set at 40 Ry, leading to a 0.05-eV convergence on the band energies. The LDA calculations were carried out in a supercell geometry, with a closest distance between nanotubes being 5 Å. This permitted us to neglect tube-tube interactions. Using the Hellmann-Feynman (HF) theorem,¹⁷ the calculated stresses imposed on each supercell along the axis direction were found negligible. In the cylindrical configuration, the HF forces are very small (< 0.05 eV/Å), and all the atoms remain equivalent within the unit cell. In a pentagonal configuration by contrast, the HF forces on the carbon atoms of the edges of the polygonal prism are much larger (~ 0.8 eV/Å). When the internal coordinates of the atoms of this configuration are relaxed using these HF forces, the cross section necessary evolves to a circle. Nevertheless, as explained before, the polygonized cross section can be constrained by external forces such as those presumably taking place in a nanotube bundle.

The TB electronic band structure and density of states shown below are deduced from a Slater-Koster Hamiltonian with parameters close to the set used for graphite in Ref. 18. There are four orbitals per atom, with the s level located at $\varepsilon_s = -7.3$ eV below the triply-degenerated p level taken as the zero of energy ($\varepsilon_p = 0$). The Slater-Koster hopping parameters for nearest-neighbor pairs are $V_{ss\sigma} = -4.30$ eV, $V_{sp\sigma} = 4.98$ eV, $V_{pp\sigma} = 6.38$ eV, and $V_{pp\pi} = -2.66$ eV. Second-neighbor interactions are taken into account using $V_{ss\sigma} = -0.18Y$, $V_{sp\sigma} = 0$, $V_{pp\sigma} = 0.35Y$, and $V_{pp\pi} = -0.10Y$, where $Y = (3.335/r_{ij})^2$ is a scaling factor depending on the interatomic distance r_{ij} (expressed in Å).

The *tight-binding* densities of states (DOS) of the (10,0) tube in both the cylindrical and pentagonal (10,0)⁵ configurations are illustrated in Fig. 1. In order to check the validity of the TB approach, *ab-initio* DOS's have also been estimated from the electron bands calculated just at the Γ and X points of the one-dimensional first Brillouin zone of the nanotube. From the LDA calculations, the (10,0) cylindrical

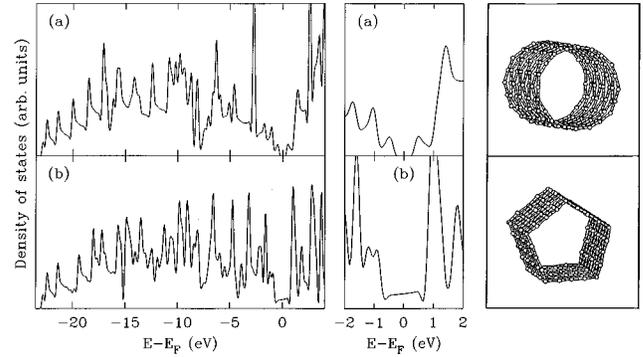


FIG. 1. *Tight-binding* densities of states (states/eV/cell) for the (10,0) cylindrical (a), and the (10,0)⁵ pentagonal (b) cross-section nanotubes. The Fermi level is positioned at zero energy. Both nanotubes are also represented in inset on the right of their respective DOS.

nanotube is found to possess a gap of 0.82 eV, and this is correctly reproduced by the TB calculations. On the other hand, the (10,0)⁵ pentagonal nanotube gap is reduced to 0.08 eV in LDA and 0.01 eV in TB. The closeness of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) bands brought about by the “polygonization” (see the band structures below) is responsible for pinning the Fermi energy at 0.0375 eV at Γ . The band gaps do not show up in the DOS of Fig. 1(b) due to the energy broadenings used, and a metalliclike plateau develops instead in the TB density of states (DOS). Both nanotube densities of states not only present the two-dimensional van Hove singularities of graphite at $E = \pm V_{pp\pi}$ (± 2.66 eV) and at $E = \pm V_{pp\sigma}$ (± 6.38 eV), but also many sharp peaks coming from the inverse square root divergence ($1/\sqrt{E}$) of the spectra of the one-dimensional (1D) bands. These singularities are due to the quantization of the 1D energy bands in the circumference direction. The LDA DOS's have not been represented as an unphysical peak appears near E_F . This is due to the lack of k points used in the *ab initio* simulation, which is also reproduced by the TB method when the same sampling set is used. Nevertheless, the presence and the location of the peaks are well described using both techniques.

For the pentagonal conformation, the DOS's calculated with both techniques in the region close to the Fermi level differ radically from that of the cylinder. The discrepancy between the electronic states of nanotubes with polygonized and circular cross sections is consistent with the notion that, in a not-too-small-radius cylinder, a good description of the nanotube electronic properties is obtained by folding the graphite sheet band structure. However, this idea implicitly relies on the assumption that states around the gap or Fermi level are essentially π - or π^* -derived.^{6,8,9} This assumption fails for nanotubes with polygonized cross sections or in very-small-radius cylindrical nanotubes,¹⁰ where the curvature is so strong (i.e., near the edges of the polygonal prism) that large σ^* - π^* hybridization occurs.

To study these effects on the low-lying state of the (10,0) nanotube, the TB band structures in the cylindrical [Fig. 2(a)] and pentagonal [Fig. 2(c)] configurations were calculated. An intermediate geometry [Fig. 2(b)] was also considered, where the sharp edge angles of the pentagonal cross

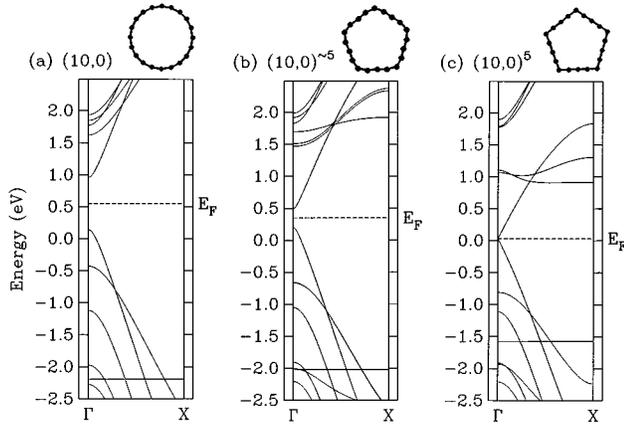


FIG. 2. Evolution of the (10,0) nanotube TB bands near the Fermi level under “polygonization” of its cross section. Pure cylindrical (a), and pentagonal (c) geometries are illustrated, separated by an intermediate configuration (b) where the sharp angles of the pentagon are smoothed using *ab initio* structural optimization (curvature radius at the corner: 2.366 Å, polynomial fit: $0.01x^4 - 0.32x^2 = 0$). The Fermi level is indicated by E_F . The shapes of the different cross sections are also illustrated on the top of the band structures.

section were smoothed using a relaxation scheme based on the *ab initio* HF atomic forces. This structural optimization process reduced the sharpness of the angles, as said above, and a smoothed cross section was extracted in the middle of the pentagon-to-circle transition path. The curvature radius present at the corner of this intermediate geometry is 2.366 Å. The energy difference between the (10,0) and (10,0)⁵ conformations was found to be of the order of 0.37 eV/atom. The evolution of the band structures of the (10,0) nanotube during “pentagonalization” is illustrated in Fig. 2, where the shapes of the cross section are also shown.

In the zigzag orientation, the σ^* and π^* singly degenerate states of a planar graphene sheet mix with each other, and not with states of higher degeneracy.¹⁰ By curving or folding the sheet, the σ^* and π^* states of the same symmetry repel each other, lowering the energy of the original π^* state. It is the lowest unoccupied hybridized π^* band which gives rise to a weakly dispersive band ~ 1 eV above the Fermi energy (E_F) in the TB band structure of Fig. 2(c). Simultaneously, a dramatic decrease of the HOMO-LUMO gap appears at Γ due to a lowering of symmetry in the pentagonal conformation, where the carbon atoms are no more identical.

The *ab initio* charge-density distributions relative to this low-lying state at the Γ point for the (10,0) and (10,0)⁵ configurations are presented in Fig. 3. For the circular cross section, the wave function is equally distributed inside and outside the tube [Fig. 3(a)], leading to state of mostly pure π^* , as an antibonding behavior has also been observed along a generator of the cylinder. By contrast, the wave function of the low-lying state of the (10,0)⁵ nanotube is anisotropic [Fig. 3(b)], with a main localization of the charge density on the edges and in the outside region of the tube. This result illustrates the partly- σ character of this state arising from the σ^* - π^* hybridization. In addition to this, the “polygonization” lowers the symmetry: all the atoms of the polygonized unit cell are no longer equivalent and the twofold degeneracy

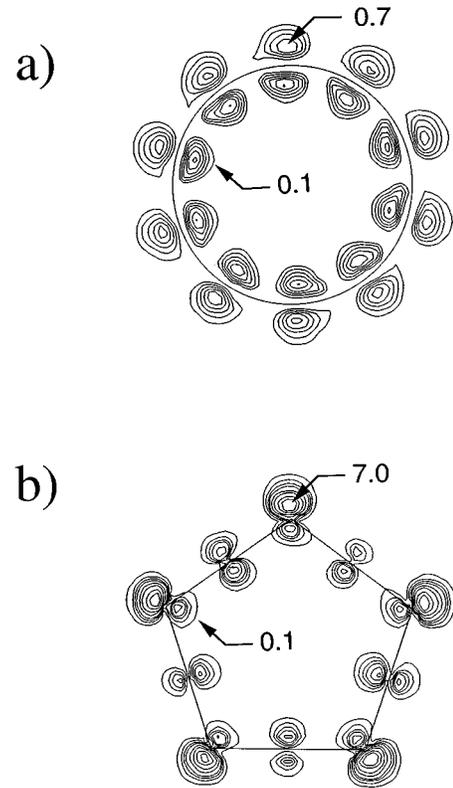


FIG. 3. Contour plot of the local electronic charge densities for the lowest unoccupied singly degenerate π^* state at Γ of the (10,0) nanotube (a), which mixes with σ^* states in the (10,0)⁵ configuration (b). The contours are drawn in a plane perpendicular to the axis of the tube which contains 10 carbon atoms. The numbers quoted are in units of $10^{-3}e/(\text{a.u.})^3$. The circle and the pentagon are guides for the eyes, representing nanotube cross sections on which the atoms lie in the (10,0) and (10,0)⁵ geometries.

of some of the bands is lifted. As mentioned previously, the significant reduction of the gap observed for the (10,0)⁵ nanotube in Fig. 2(c) is concomitant to all of these effects.

Metallic zigzag nanotubes [($n,0$) where n is a multiple of 3] with different polygonized cross sections were also investigated. The TB band structures of (12,0)³, (12,0)⁴, and (12,0)⁶ are shown in Fig. 4 where they are compared to that of a perfect cylindrical-shaped (12,0) nanotube. All kinds of electronic properties arise: the first two cases are metals, the (12,0)⁶ is a 0.5-eV-gap semiconductor, whereas the cylindrical (12,0) nanotube is metallic. In the zigzag symmetry, the “polygonization” induces both curvature and lowering symmetry effects which leads the π - π^* crossing point in the graphene sheet band structure to move forward from the K point, and reach a line of allowed eigenvectors imposed by periodic boundary conditions along the circumference of the nanotube. This perturbation generates various electronic properties like a quasimetallic nanotube in the (10,0)⁵ case [Fig. 2(c)], and a semiconducting one in the (12,0)⁶ topology [Fig. 4(c)], in opposition with the electronic behaviors predicted for the two respective cylindrical conformations [Fig. 2(a) and Fig. 4(d)].

In the armchair configuration, not illustrated here, polygonizing the section of the nanotube has much less pronounced effects on the band structure. In the cylindrical ge-

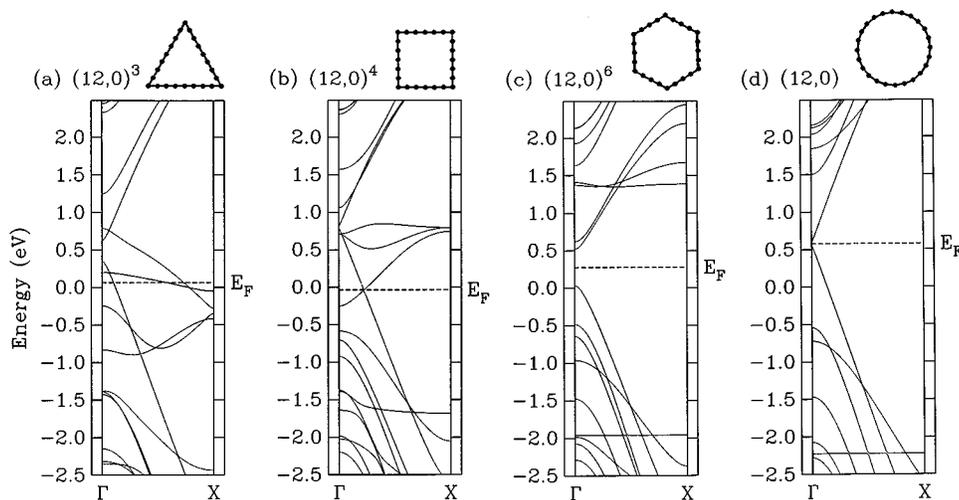


FIG. 4. Tight-binding band structures of the metallic $(12,0)$ nanotube, illustrating the effect of the degree of polygonization of the cross section on the electronic behavior. Triangle, $(12,0)^3$ (a); square, $(12,0)^4$ (b); and hexagonal, $(12,0)^6$ (c) geometries are presented and compared to the pure cylinder case (d). The shapes of the different cross sections are also included on the top of the respective band structures.

ometry, the σ^* and π^* singly degenerate states are much more separated than with the zigzag arrangement, leading to a very small hybridizing interaction between them. No low-lying band is perturbing the HOMO-LUMO crossing point appearing at the $\frac{2}{3}$ of the $\Gamma-X$ direction⁸ and all the nanotubes considered remained metallic upon “polygonization,” except for a triangular cross section of the $(6,6)$ system, where a small gap of 0.4 eV is lifted.

In conclusion, polygonizing the section of zigzag carbon nanotubes induces curvature (σ^* - π^* hybridization) and lowering symmetry effects which drastically change the electronic band structure from that obtained by simply “folding” the graphene sheet band structure. An implication of this result is that hybridization effects could also play an important role on the electronic properties of a solid-state packing of faceted nanotubes, which one-dimensional chan-

nels (either inside or outside the tubes) are accommodated with a single atomic row of intercalant atoms. As metallic armchair nanotubes are less affected, one can wonder about the possibility of synthesizing insulating or wide-gap semiconducting carbon tubes, with important consequences to the transport properties of these mesoscopic systems.¹⁹

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