Band structure and optical properties of isolated and bundled nanotubes

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Abstract. We studied the electronic band structure of isolated and bundled single-walled nanotubes by *ab initio* calculations. Curvature effects on the electronic states depend on the chirality of the nanotube; the strongest deviations from the zone-folding approximation are found in zig-zag tubes. Bundling of the tubes to ropes further reduces the band gap in semiconducting tubes (20 - 30 %). We present first-principles calculations of the optical absorption spectra in a (19,0) nanotube.

When a graphene sheet is rolled up to a nanotube the mirror symmetry perpendicular to the sheet is broken. Therefore, the π and σ states of graphene are allowed to mix, which lowers the energies of the π derived nanotube states.[1, 2] At the same time, the rolling up introduces m, the z component of the angular momentum, as a conserved quantum number, since a tube is essentially a linear molecule extending infinitely along the z axis.[3] The hybridization of the σ and π orbitals is usually assumed to be negligible for realistic nanotubes ($d \approx 1.5\,$nm). In Ref. [2] we showed, however, that curvature effects depend both on the diameter and the chirality of a nanotube.

In this paper we complete the task of Ref. [2] by comparing the *ab initio* band structure for a (10,10) armchair tube and a (19,0) zig-zag tube with the corresponding zone-folding and tight-binding results. Whereas the first-principles band structure of the armchair tube is perfectly described by zone folding, the electronic states in the optical regime are shifted by as much as 100 meV in the (19,0) zig-zag tube. Bundling of the tubes to ropes splits the doubly degenerate electronic states and introduces an electronic dispersion perpendicular to the nanotube axis. We show first-principles optical absorption spectra of a (19,0) tube and discuss the selection rules for dipole transitions.

Ab initio calculations with SIESTA[4, 5] were performed within the local density approximation[6]. Pseudo potentials[7] replaced the core electrons, while the valence states were expanded in a double-ζ basis set plus polarizing orbitals.[8] The cutoff radii of the basis functions were 5.12 a.u. for the s and 6.25 a.u. for the p and d orbitals. Real space integrations were performed on a grid corresponding to a cutoff of $\approx 270\,$Ry. In isolated armchair (zig-zag) nanotubes we used 30 (10) k-points in reciprocal space to find the total energy; the bundled tubes were calculated on a $10 \times 10 \times 30$ Monkhorst-Pack grid.[9] The band structure was obtained by calculating the eigenenergies of the Kohn-Sham Hamiltonian at 60 (45) points in reciprocal space along the armchair (zig-

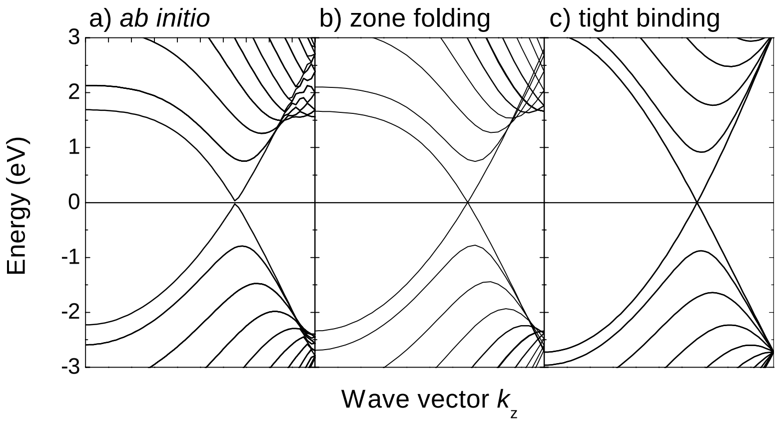

FIGURE 1. Band structure of a (10,10) armchair nanotube; (a) *ab initio* calculation, (b) zone-folding of graphene, and (c) π orbitals nearest-neighbor tight-binding calculation with $\gamma_0 = -2.7\,\text{eV}$. The largest difference in energy for an electronic state in a) and b) is 40 meV.

zag) nanotube axis. 30 k points were used along the $\Gamma KM\Gamma$ lines of the Brillouin zone in bundled tubes. Finally, the eigenvectors and energies were found at 120 k points along the z axis. These eigenvalues were used to calculate the imaginary part of the dielectric function by first-order perturbation theory.[5]

Figure 1a) shows the *ab initio* band structure of a (10,10) nanotube ($d = 1.57\,\text{nm}$). To study curvature effects we plot in Fig. 1b) the zone-folding band structure, i.e., neglecting the rolling up, of the (10,10) tube. We obtained the zone-folded electronic dispersion from an *ab initio* calculation of graphene using the same approximations as described for the tubes above. The agreement between the first-principles and the zone-folding approximation is excellent for a (10,10) nanotube. In armchair tubes of this diameter curvature effects can thus be neglected when studying the electronic properties within 3 eV of the Fermi level.[2] The nearest-neighbor tight-binding approximation of

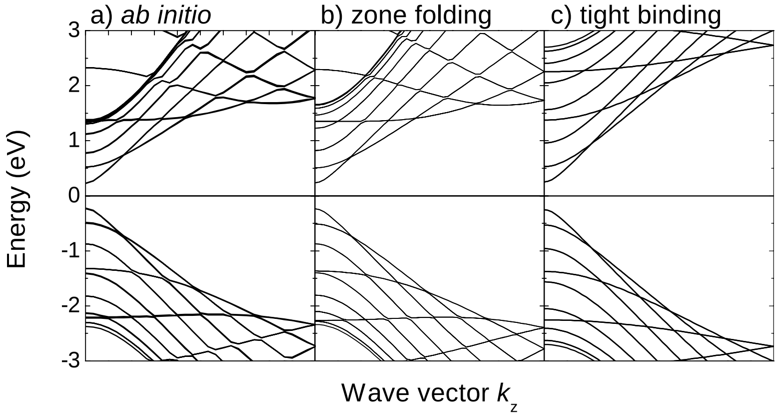

FIGURE 2. Band structure of a (19,0) zig-zag nanotube; (a) *ab initio* calculation, (b) zone-folding of graphene, and (c) π orbitals nearest-neighbor tight-binding calculation with $\gamma_0 = -2.7\,\text{eV}$. The largest difference in energy for an electronic state in a) and b) is 280 meV.

the graphene π orbitals in Fig. 1c), however, rather poorly describes the band structure of the (10,10) tube. This failure is due to the fact that this simple description already fails in reproducing the *ab-initio* results of graphene. In Fig. 2 we show the same calculations for the (19,0) zig-zag as for the (10,10) armchair tube in Fig. 1. For zig-zag tubes zone folding correctly predicts only the two valence and conduction bands closest to the Fermi level. The conduction bands involved in optical transitions in the visible energy range are shifted to lower energies by as much as 100 meV. The chirality dependence of the hybridization effects come from the chirality dependence of the confinement direction with respect to graphene as we discussed in Ref. [2].

Bundling of the tubes to ropes, in general, shifts the Γ point electronic energies towards the Fermi level. More importantly, however, the coupling between the tubes gives rise to an intertube dispersion perpendicular to the z axis. As a typical example we show in Fig. 3 the band structure of a bundle composed of (19,0) nanotubes along the $\Gamma M K \Gamma$ high-symmetry lines of the Brillouin zone. At the Γ point the lowest lying conduction and valence band in the isolated tubes are split by 135 and 504 meV, respectively. The black dots in Fig. 3 mark the position of the Γ point energies in the isolated (19,0) tube, see Fig. 2. The width of the intertube electronic bands is on the order of 100 meV, very similar to graphene and solid C_{60}.[10, 11] The intertube dispersion strongly broadens the square-root singularities in the electronic density of states and reduces the band gap by $20-30\,\%$ in semiconducting nanotubes. Note that the (19,0) bundle is an indirect semiconductor with a band gap energy of only 40 meV, see Fig. 3.

Finally, we show in Fig. 4 the absorption spectrum of an isolated (19,0) nanotube. Full (dashed) lines correspond to the incoming light polarized parallel (perpendicular) to the tube z axis. Under parallel polarization we find a series of singularities in the absorption coefficient. A very similar result is obtained by simply considering the joint density of electronic states in the (19,0) nanotube for bands with the same m quantum number (i.e., the valence and conduction band being approximately symmetric with respect to the Fermi level). Up to ≈ 4 eV the singularities originate solely from the Γ point of the nanotube Brillouin zone. At 3.9 eV transitions coming from the Brillouin zone boundary give rise to a first singularity in the joint density of states and thus the absorption spectrum in parallel polarization. The situation changes drastically for incoming light polarized perpendicular to the tube axis. Below ≈ 3.5 eV the absorption

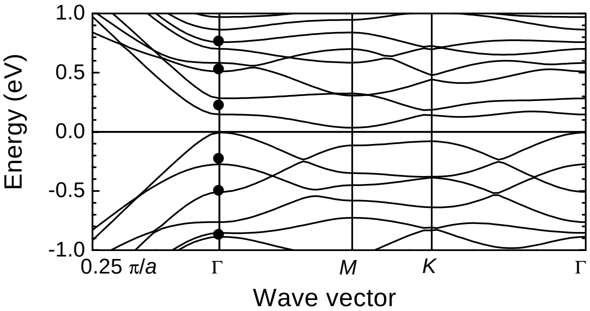

FIGURE 3. Intertube dispersion in a (19,0) nanotube. The (19,0) bundle is an indirect semiconductor with a band gap of 40 meV. The black dots indicate the electronic energies at the Γ point of the isolated (19,0) nanotube.

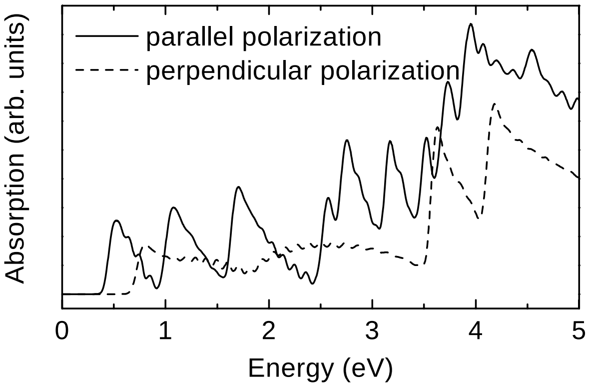

FIGURE 4. Absorption coefficient α in a (19,0) nanotube. Full lines are for the incoming light polarized parallel to the nanotube axis; dashed lines for perpendicular polarization. The horizontal mirror symmetry in achiral tubes forbids transitions at the Γ point for perpendicularly polarized light except for the valence and conduction band pairs being most closely to the Fermi energy.

spectrum is now flat and unstructured; at 3.62 eV transitions between electronic states in the interior of the Brillouin zone begin contributing to the spectrum. The differences between the two polarizations are a consequence of the stringent selection rules at the Γ point of the Brillouin zone: For perpendicularly polarized light optical transitions take place between valence and conduction band differing by ±1 in their m quantum number. If, additionally, the horizontal mirror parity is considered, dipole transitions are forbidden at the Γ point in zig-zag nanotubes except for the first two pairs of valence and conduction bands (referred to the Fermi level). These pairs give rise to the weak singularity below 1 eV in Fig. 4. A more detailed discussion of the optical properties of carbon nanotubes, in particular, of bundled tubes will be published elsewhere.

In conclusion, we studied the electronic band structure in achiral tubes with $d \approx 1.5\,\mathrm{nm}$. For armchair tubes zone folding correctly predicts the electronic band structure, whereas the energies still differ in zig-zag tubes. We discussed the effect of bundling on the electronic properties of carbon nanotubes and presented first *ab initio* results for the optical absorption in this one-dimensional system.

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