



The curvature of the nanotube sidewall and its effect on the electronic and optical properties of zigzag nanotubes



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ABSTRACT

In this paper, we employ the density functional theory to perform a thorough study of the impact of the nanotube sidewall curvature on the optical properties by investigating several effects arising from this curvature, such as σ - π orbital rehybridization, the carbon-carbon bond length, and the mixing of d and p orbitals. Separating these and studying their effects independently, provides insight into the reasons behind the different values obtained for optical transition energies in experiments and in tight-binding/zonefolding calculations, where the curvature of the nanotube sidewall is neglected. As well, it is useful in the understanding of how and to what extent each of these effects are responsible for the accurate prediction of the electronic and optical properties of carbon nanotubes. Although the σ - π rehybridization is known as the main curvature effect in the literature, we show that the effect of bond length is quite significant as well and needs to be properly taken into account. For example, the first transition energy (E_{11}) of a (4,0) nanotube is decreased by $\sim 64\%$ and $\sim 46\%$ due to σ - π rehybridization and bond length effect, respectively. Another important observation is that the overall effect of σ - π rehybridization and bond length does not have a monotonous diameter dependence. Rather, our study suggests a dependence on the nanotube index, n , since zigzag nanotubes with $n(\text{mod})3 = 1$ show a different behavior compared to the ones with $n(\text{mod})3 = 2$. We also show that for some of the nanotubes, the effect of including the d orbitals on the optical transition energies can be as significant as the effect of σ - π orbital rehybridization and bond length. Due to the importance of the bond length effect, we also investigate several methods of geometry optimization for nanotubes. It appears that the HSEH1PBE functional might lead to the most accurate prediction of the nanotube geometry compared to the other functionals tested.

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1. Introduction

The optical absorption properties of carbon nanotubes (CNTs) have been widely investigated using experiments and theoretical calculations [1–6]. A strong connection between the absorption behaviour and nanotube diameter has been observed. Therefore, understanding the effect of the diameter on the electronic structure and absorption properties is essential. Measurements of the optical transition energies for nanotubes with small diameters [1] have yielded values significantly different from the theoretical values predicted with the tight-binding (TB) method [7]. This is mostly due to the fact that the results reported in [7] are based on the zone-folding (ZF) approximation of graphene, where the curvature of the nanotube sidewall is neglected. The effect of this curvature becomes increasingly important as the diameter of nanotube decreases and, therefore, neglecting it can result in significant calculations errors for small-diameter nanotubes. Although general discussions about the importance of the nanotube sidewall

curvature exists in the literature, a thorough study of several effects arising from this curvature and their impacts on the optical transition energies is missing. Here, we perform a detailed study of the nanotube sidewall curvature by examining the affects of σ - π orbital rehybridization, the carbon-carbon (C-C) bond length, and the mixing of d and p orbitals, separately. The goal is to investigate how and to what extent each of these can affect the optical transition energies and to understand which ones are crucial in accurately predicting the electronic and optical properties of carbon nanotubes.

We employed the density functional theory (DFT) to calculate the electronic structure of zigzag nanotubes. Geometry optimization, as well as the calculation of the orbital energies and wave functions were performed in Gaussian 09 [8]. We obtained the transition rate spectra by calculating the dipole moments and using Fermi's golden rule (details of the methodology can be found in Ref. [9]). The polarization of light was assumed to be parallel to the nanotube axis. The method described in Ref. [9] enables a thorough, broad-range study of the band-to-band optical transitions. Also, by using DFT, curvature and many-body effects (that are ignored in TB/ZF) are automatically included in the calculations.

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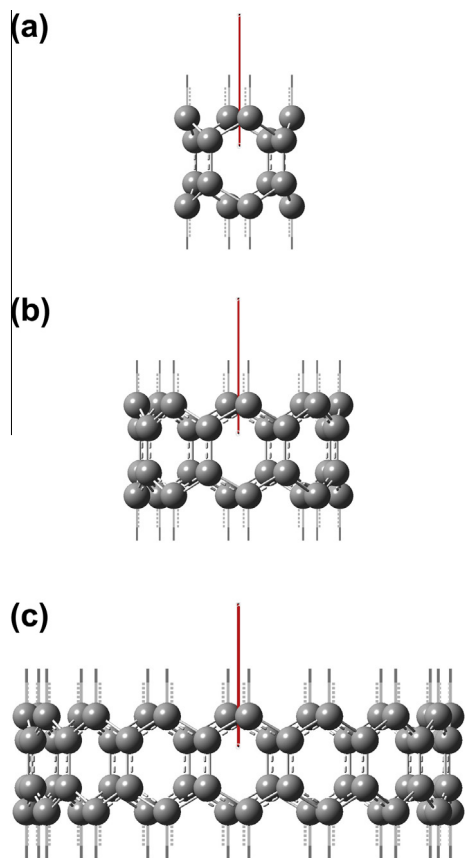


Fig. 1. One unit cell of (a) a (4,0) (b) an (8,0), and (c) a (16,0) nanotube with diameters of ~ 0.34 , ~ 0.63 , and ~ 1.27 nm, respectively. The nanotube axis is vertical in all cases.

2. DFT vs. TB/ZF and σ - π rehybridization

We simulated (4,0), (8,0), and (16,0) nanotubes with significantly different diameters (~ 0.34 , ~ 0.63 , and ~ 1.27 nm, respectively) in order to capture the effect of diameter and curvature (Fig. 1). In this section, we present the results for nanotubes prior to geometry optimization, i.e. nanotubes for which all the C–C bonds have a length equal to that in graphene (1.42 Å). In the next section, we compare the results before and after geometry optimization to show the effect of bond length.

Rehybridization of the σ and π orbitals, as one result of the nanotube sidewall curvature, can significantly affect the electronic structure of nanotubes with small diameters [10]. Fig. 2 shows the band structure of the (4,0), (8,0), and (16,0) nanotubes as calculated by TB/ZF (with hopping energy of 2.7 eV) and DFT calculations using BLYP [11,12] exchange–correlation functional and the 6-31G basis set. The difference between the two band structures increases progressively as the nanotube diameter decreases. In particular, the singly degenerate conduction band (α) in the DFT band structure is shifted down significantly for all three nanotubes compared to the one predicted by TB/ZF [10]. For an (8,0) nanotube, this downshifting places the (α) band in the band gap, resulting in a smaller gap (0.79 eV) compared to the one predicted by the TB/ZF method (1.27 eV). This band is shifted down even further to below the fermi level for a (4,0) nanotube, leading to metallic properties for this nanotube. As can be seen in Fig. 2, the DFT valence bands are mostly shifted up compared to the TB/ZF bands.

Table 1 shows a comparison of the first two optical transition energies obtained from our DFT and TB/ZF calculations. It is important to note that not only the transition energies but also the order

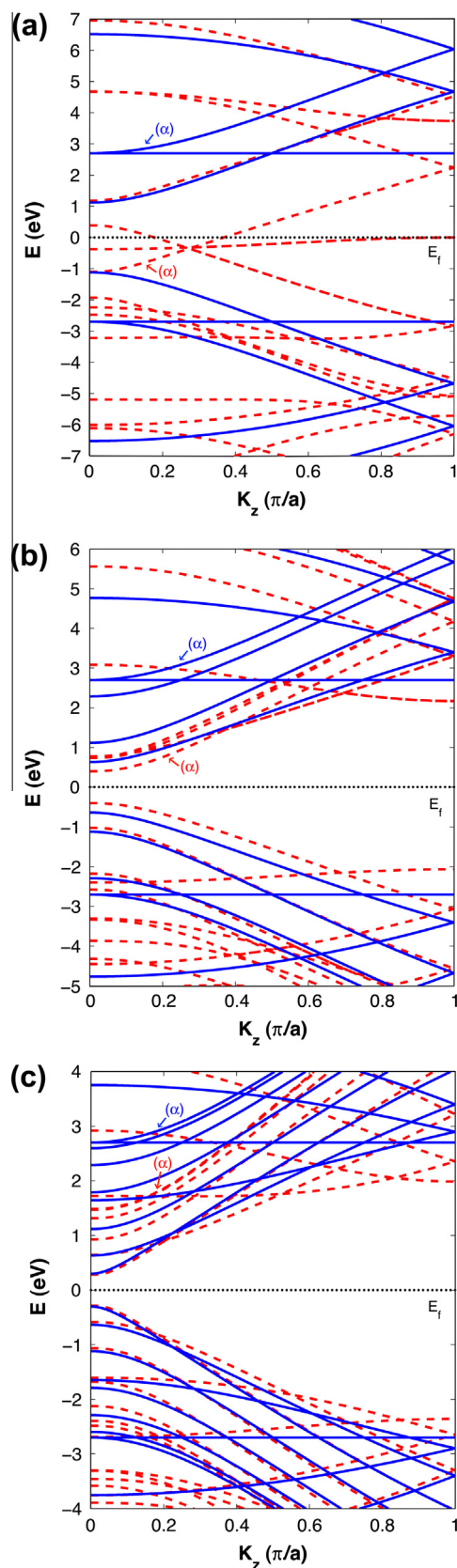


Fig. 2. Electronic band structure of (a) a (4,0) (b) an (8,0), and (c) a (16,0) nanotube with TB/ZF (solid blue) and BLYP/6-31G (dashed red) calculations. The geometries of nanotubes are not optimized. The singly degenerate band (α) is predicted for both band structures. The fermi level is at zero. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1

Comparison of the lowest two optical transition energies calculated with TB/ZF and BLYP/6-31G. The energy change compared to TB/ZF results is denoted by Δ .

		E_{11} (eV)	Transition	E_{22} (eV)	Transition
(4,0)	TB/ZF	2.24	v1 \rightarrow c1	5.40	v2 \rightarrow c2
	BLYP/6-31G	0.80	v1 \rightarrow c1	5.04	v2 \rightarrow c2
	Δ	-64.29%		-6.67%	
(8,0)	TB/ZF	1.27	v1 \rightarrow c1	2.24	v2 \rightarrow c2
	BLYP/6-31G	1.18	v1 \rightarrow c4	1.78	v2 \rightarrow c3
	Δ	-7.08%		-20.54%	
(16,0)	TB/ZF	0.60	v1 \rightarrow c1	1.27	v2 \rightarrow c2
	BLYP/6-31G	0.57	v1 \rightarrow c1	1.23	v2 \rightarrow c2
	Δ	-5.00%		-3.15%	

Table 2

The CC_1 and CC_2 bond lengths (parallel and perpendicular to the nanotube axis, respectively) after geometry optimization with BLYP/6-31G.

Nanotube	CC_1 (Å)	CC_2 (Å)	CC_2/CC_1
(4,0)	1.399	1.501	1.073
(8,0)	1.429	1.451	1.015
(16,0)	1.436	1.440	1.003

of some of the transitions are different between the two methods. The reduction of E_{11} values in the DFT calculations are mainly due to the upshifting of the first valence band. The corresponding conduction bands are almost at the same energy as the ones calculated in TB/ZF. ΔE_{11} increases as the diameter decreases due to the stronger shift of the first valence band in smaller nanotubes. We do not see the same diameter dependence for ΔE_{22} . For an (8,0) nanotube the upshift of the second valence (v2) and downshift of the third conduction (c3) bands both account for the significantly smaller E_{22} (v2 \rightarrow c3 transition) energy compared to the TB/ZF energy. For a (4,0) nanotube, on the other hand, E_{22} is not significantly different between the two methods. This is due to the fact that the dispersionless second valence (v2) and second conduction (c2) bands in the DFT band structure of a (4,0) CNT are both shifted up with respect to the TB/ZF bands by almost the same amount.

3. Effect of the C–C bond length

Another important consideration is that the C–C bond lengths in nanotubes are different from the ones in a graphene sheet due to the curvature of the nanotube sidewalls. For zigzag nanotubes, this curvature results in two different bond lengths; one is the C–C bond length parallel to the nanotube axis (CC_1) and the other is the one around the nanotube circumference (CC_2), with CC_2 being longer than CC_1 due to the weakening of the strained bonds wrapped around the nanotube [13,14]. Table 2 shows the CC_1 and CC_2 bond lengths after geometry optimization using BLYP/6-31G. The CC_2/CC_1 ratio shows that the two bond lengths approach each other as the diameter of the nanotube increases.

Fig. 3 shows the comparison for the band structures of the three nanotubes before and after geometry optimization. Significant changes to some of the bands can be observed after geometry optimization, and the values in Table 3 indicate substantial differences in the transition energies for almost all the cases, in the same order as or even larger than the changes discussed in the previous section (Table 1 values).

This time, the further reduction of E_{11} for (4,0) and (16,0) nanotubes is due to the downshift of the first conduction band. For an (8,0) nanotube, the opposite mechanism happens; the first valence

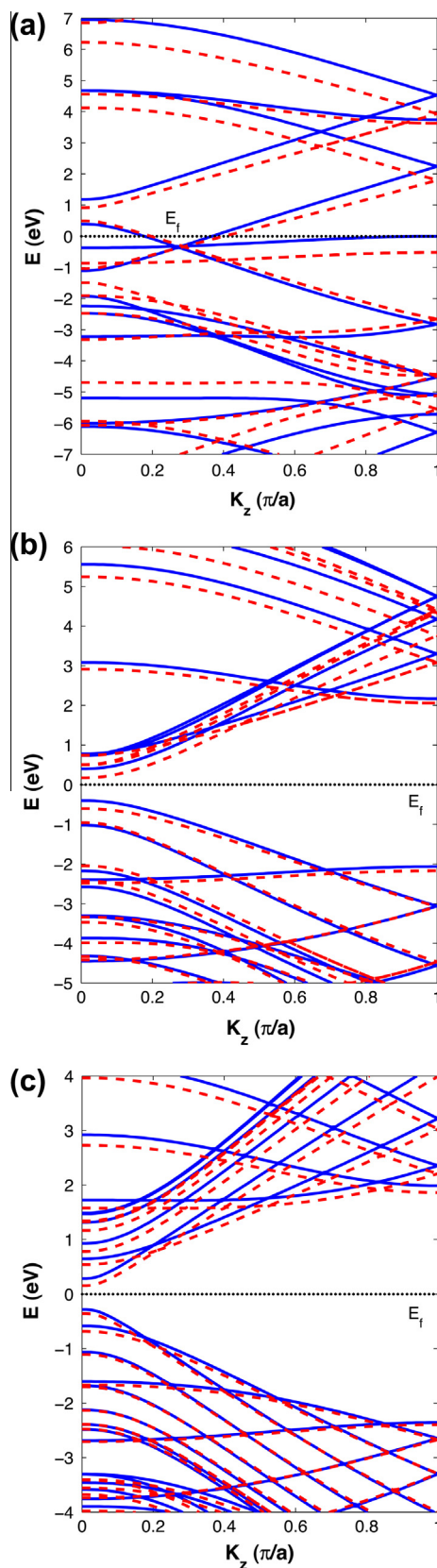


Fig. 3. Electronic band structure of (a) a (4,0) (b) an (8,0), and (c) a (16,0) nanotube without (solid blue) and with (dashed red) geometry optimization. The geometries and the band structures are calculated with BLYP/6-31G. The Fermi levels are based on the calculations prior to the geometry optimization. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 3

Comparison of the lowest two optical transition energies, calculated by BLYP/6-31G before and after the geometry relaxation. The energy change after geometry optimization is denoted by Δ .

		E_{11} (eV)	Transition	E_{22} (eV)	Transition
(4,0)	Before relaxation	0.80	v1 → c2	5.04	v2 → c3
	After relaxation	0.43	v1 → c2	5.43	v2 → c4
	Δ	-46.25%		7.74%	
(8,0)	Before relaxation	1.18	v1 → c4	1.78	v2 → c3
	After relaxation	1.35	v1 → c4	1.46	v2 → c3
	Δ	14.41%		-17.98%	
(16,0)	Before relaxation	0.57	v1 → c1	1.23	v2 → c2
	After relaxation	0.52	v1 → c1	1.23	v2 → c2
	Δ	-8.77%		0	

Table 4

The difference between the results obtained using DFT calculations after geometry optimization and the TB/ZF results.

Nanotube	ΔE_{11} (%)	ΔE_{22} (%)
(4,0)	-80.80	0.56
(8,0)	6.30	-34.82
(16,0)	-13.33	-3.15

band is shifted down, leading to a larger value for E_{11} and the downshift of the c3 band results in the reduction of E_{22} . Both in here and also in Table 1, we can see trends that are oscillating with diameter rather than having a monotonous diameter dependence. The overall effect of DFT calculations and bond length (Table 4) also, shows the same trend, which in turn, suggests the dependence of these effects on the zigzag nanotube index, n . Our calculations for various other zigzag nanotubes confirms this point. Fig. 4 shows the plots of ΔE_{11} and ΔE_{22} versus the nanotube index. We see that nanotubes with $n(mod)3 = 1$ have a different behaviour compared to the ones with $n(mod)3 = 2$.

The importance of the effect of bond length on the electronic and optical properties, in turn, points out to the importance of the method of geometry optimization for carbon nanotubes and raises the question: what method can predict the geometry of the nanotubes most accurately and what is the sensitivity of the absorption properties on the method of relaxation? This is particularly important since for many nanotubes there are no experimental data on bond lengths.

The Hartree–Fock (HF) method is known to underestimate the bond lengths while DFT approaches with GGA (generalized gradient approximation) functionals generally overestimate bond lengths [15]. Consequently, one might think that hybrid methods can provide a closer estimate to the experimental values of bond lengths. To investigate this, we performed a series of simulations using different functionals on graphene, for which the experimental value of the bond length is available. Table 5 summarizes the C–C bond lengths obtained for graphene. It can be seen that HSEH1PBE, which is a hybrid method, yields a more reasonable value (closer to the experimental value) for the bond length of graphene compared to the others. By extension, we suggest that this method will be more accurate for nanotubes as well. In Table 6 we compare the (8,0) nanotube C–C bond lengths calculated with BLYP/6-31G and HSEH1PBE. Table 7 also, shows the first two optical transition energies calculated for an (8,0) nanotube that is optimized by HSEH1PBE/6-31G, compared against the values obtained from BLYP/6-31 optimized nanotubes. As we see, although the first optical transitions have similar values for the two nanotubes, the second optical transitions show to be dependent on the method of geometry relaxation.

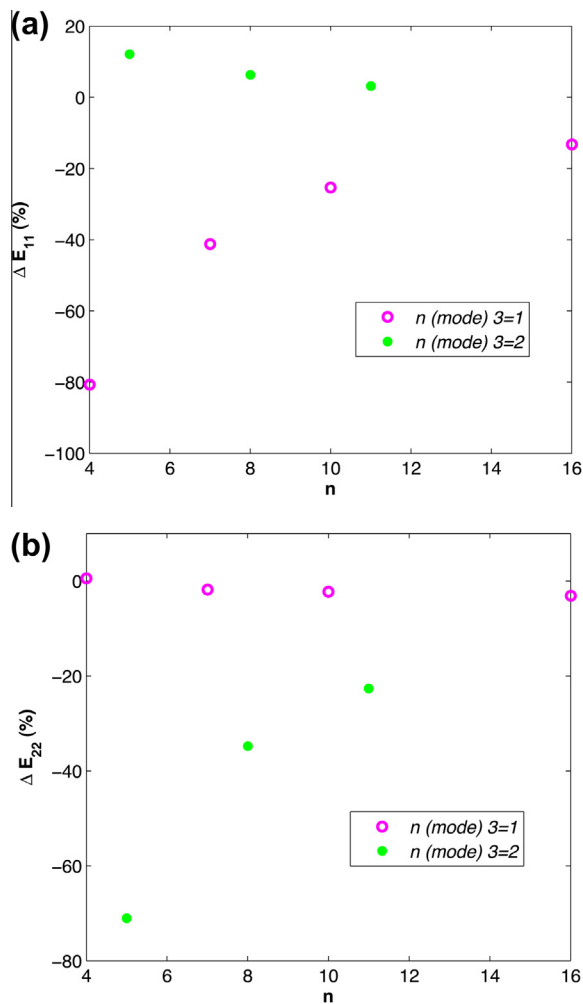


Fig. 4. Plot of the difference between the first (a) and second (b) transition energies (ΔE_{11} and ΔE_{22} , respectively) for BLYP/6-31G calculations (after geometry optimization) of $(n,0)$ nanotubes and their corresponding TB/ZF values. Values for nanotubes with $n(mod)3 = 1$ are shown in purple (empty) circles and the ones with $n(mod)3 = 2$ are shown in green (solid) circles. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 5

Comparison of the C–C bond length in graphene calculated with different methods.

Method	C–C bond length (Å)
Experimental	1.421
BLYP/6-31G	1.436991
PW91PW91/6-31G	1.430848
PBEPBE/6-31G	1.431983
HSEH1PBE/6-31G	1.421419
V5XC/6-31G	1.432008

Table 6

Comparison of the C–C bond lengths in an (8,0) nanotube calculated with BLYP and HSEH1PBE methods.

Method of geometry optimization	CC_1 (Å)	CC_2 (Å)
BLYP/6-31G	1.429	1.451
HSEH1PBE/6-31G	1.414	1.433

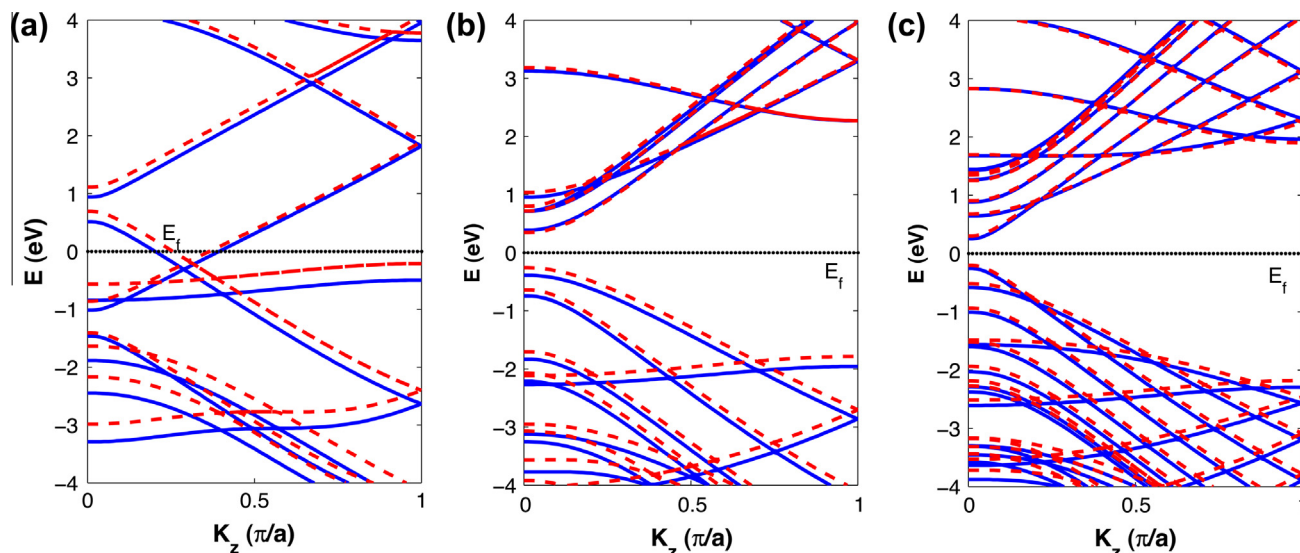


Fig. 5. Band structure with BLYP/6-31G (solid blue) and BLYP/6-31G(d) (dashed red) for (a) (4,0), (b) (8,0) and (c) (16,0) nanotubes. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 7

Comparison of the first two optical transition energies for an (8,0) nanotube that is geometry optimized with BLYP and HSEH1PBE methods. The electronic structure has been calculated using BLYP/6-31G in both cases.

Method of geometry optimization	E_{11} (eV)	E_{22} (eV)
BLYP/6-31G	1.35	1.46
HSEH1PBE/6-31G	1.37	1.53

4. Mixing of d and p orbitals

The mixing of d and p orbitals, as one other consequence of nanotube curvature, has been discussed in some works [16]. Fig. 5 shows the band structures calculated using BLYP/6-31G and BLYP/6-31G(d) for (4,0), (8,0), and (16,0) nanotubes. While improvement is expected by the inclusion of the d orbitals, we would like to investigate the level of improvement and its dependence on the diameter. Furthermore, we would like to study the impact of this inclusion on the optical transition energies. We see from Fig. 5 that the valence bands are in general more affected by inclusion of the d orbitals compared to the conduction bands. Moreover, the effect is stronger for smaller-diameter nanotubes due to the stronger mixing of the orbitals at higher curvature. The first two optical transition energies calculated with BLYP/6-31G and BLYP/6-31G(d) are shown in Table 8. Interestingly, again an oscillating behaviour can be seen for both ΔE_{11} and ΔE_{22} as a function of nanotube index. While the effect of d orbitals on some

Table 8

Comparison of the lowest two optical transition energies with and without including the d orbitals. Δ is the energy difference.

		E_{11} (eV)	E_{22} (eV)
(4,0)	BLYP/6-31G	0.43	5.43
	BLYP/6-31G(d)	0.42	5.31
	Δ	-2.11%	-2.23%
(8,0)	BLYP/6-31G	1.35	1.46
	BLYP/6-31G(d)	1.30	1.44
	Δ	-3.57%	-1.64%
(16,0)	BLYP/6-31G	0.52	1.23
	BLYP/6-31G(d)	0.51	1.20
	Δ	-1.16%	-2.53%

of the transitions might seem negligible, for certain transitions the energy difference is comparable to if not larger than the difference caused by other effects discussed in this paper (*cf.* Table 4), and therefore, important to include.

5. Summary

We investigated several effects caused by the curvature of the nanotube sidewall and their consequences on the electronic and optical properties of zigzag nanotubes. Although in the literature, the effect of curvature is mainly attributed to σ - π rehybridization, we showed that both the σ - π rehybridization and bond length effects are crucial in the accurate prediction of the optical transition energies of small-diameter nanotubes. Transition energies predicted by DFT showed to differ significantly from the ones by TB/ZF calculations (up to ~64%) and the effect of bond length by itself resulted in substantial differences for most E_{11} and E_{22} energies (up to ~46%). The overall effect on the transition energies showed to depend on the nanotube index, n , rather than the diameter. We confirmed this by plotting the differences against the nanotube index for several nanotubes. Nanotubes with $n(\text{mod})3 = 1$ showed a different behaviour compared to the ones with $n(\text{mod})3 = 2$. For some of the transitions, the effect of the mixing of d and p orbitals due to the curvature turned out to be as significant as the effect of σ - π rehybridization and bond length. Finally, the importance of the effect of bond length prompted a study on the method of geometry optimization. Among all the methods tested, our DFT calculations using HSEH1PBE functional yielded the most accurate prediction for the C-C bond length of graphene. The study presented in this paper can provide insight into the significance of several individual effects arising from the nanotube sidewall curvature and the level of improvement that including each of these effects can bring into the theoretical calculations.

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