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Abstract
An efficient and reasonable procedure is proposed for calculating the electronic
structure of carbon nanotori in terms of rotational symmetry, within the tight
binding formalism. It is shown that the curvature induced σ^*–π^* hybridization
effects play an important role in determining the electronic structure of this
novel nanostructure. The energy gap of the carbon nanotorus exhibits a well
defined oscillation feature with increasing size of the torus, converging to that of
the corresponding infinite nanotube, while its density of states spectrum evolves
from the characteristic of a zero dimensional system to that of a quasi-one
dimensional system. Effects of disorder on the electronic properties are also
discussed.

1. Introduction

Since the discovery of carbon nanotori [1], many experimental and theoretical efforts have
focused on the properties of these novel carbon nanostructures [2–11], suggesting potential
application for this nanometre sized electromagnetic element. Of special interest is the
electronic structure of this toroidal system, which has been addressed in several corresponding
works [5, 7, 10, 11]. For the graphite-like nanostructures, it is demonstrated that strong
hybridization effects can occur because of the existence of high curvature, and thus play
an important role in determining the electronic structure [12, 13]. As regards the finite
sized and ring shaped carbon nanotorus, which can be formed by bending around a single
nanotube and connecting its two ends, the curvature is rather more complicated than that of the
corresponding straight carbon nanotube, since the former has not only a highly curved surface
but also nonuniform bond length. Therefore, one can expect the curvature and hybridization
to have pronounced effects on the electronic structure of this ring shaped carbon nanotorus.

However, the importance of these effects was not fully appreciated in previous calculations. For example, the persistent currents in carbon nanotori were investigated theoretically [5], where the electronic structure of this system was obtained by the simplest zone-folding approach; while in exploring the electronic and magnetic properties of this carbon nanotorus [7, 10, 11], the single π tight binding (TB) model was usually adopted for simplicity. Using these simple models to describe the electronic structure of this ring shaped molecule is at the cost of neglecting the specific curvature and hybridization effects. The lack of a sound treatment of this problem is mainly due to the complexity of the carbon nanotorus structure, such as it having no translational symmetry but a relatively large number of atoms, which forms the major challenge in calculating the electronic structure, whether by empirical or first principles simulations. From the theoretical point of view, it is greatly desirable to explore the electronic structure of carbon nanotori in an efficient and reasonable approach, via which one can fully take into account both the curvature and hybridization effects. This is the main task of this work. Additionally, the disorder effects on the electronic properties are also discussed. It may be expected that such an exploration can provide a much better understanding of the physical properties of carbon nanotori as well as a typical way to describe similar structures.

2. Model and method

In this work, we calculate the electronic structure of carbon nanotori within the empirical TB formalism. Note that the disorder is not included in the following formalism. The tight binding Hamiltonian, considering only the s and p valence electrons of the carbon atom, is given by

$$H = \sum_{i,\alpha} \epsilon_\alpha a_{i,\alpha}^+ a_{i,\alpha} + \sum_{i,j,\alpha,\beta} t_{\alpha\beta}(r_{ij}) a_{i,\alpha}^+ a_{j,\beta}. \tag{1}$$

Here, i labels the atomic site and $\alpha = s, p_x, p_y, p_z$ labels the atomic orbital. ϵ_α is the orbital energy and $t_{\alpha\beta}$ the matrix elements for hopping between different orbitals. We adopt the parameters given in [13] to model the nearest neighbour and the second neighbour interactions. Considering the variations of the bond length, the hopping matrix elements for nearest neighbour atoms are multiplied by a modified factor

$$f(d_{ij}) = (1 + \lambda d_{ij}) e^{-\lambda(d_{ij} - d_0)}/(1 + \lambda d_0), \tag{2}$$

with $\lambda d_0 = 2.732$, d_{ij} and d_0 the nonequilibrium and equilibrium separation respectively [15]. For the second neighbour interactions, we follow the corresponding parameters and scaling factor given in [13]. The wavefunction can be constructed from linear combination of the atomic orbital wavefunctions, i.e.,

$$|\Psi\rangle = \sum_{i,\alpha} C_{i,\alpha} |i, \alpha\rangle. \tag{3}$$

Following the notation of [5], we take the index (n, m, p) to define a carbon nanotorus, formed from a finite length single wall carbon nanotube (n, m) containing p unit cells. In terms of the rotational symmetry, one needs only find the positions of the atoms in one unit cell to determine the positions of all the atoms on the torus. For simplicity, this work mainly focuses on achiral type nanotori, i.e., (n, n, p) and $(n, 0, p)$. For an armchair type (n, n, p) torus, each unit cell consists of two atomic rings, while there are four atomic rings in one unit cell of a zigzag type $(n, 0, p)$ torus. The relative position of each atom located in the same atomic ring can be obtained, and the direction cosines and length of the position vector r_{ij} are then defined for calculating the hopping integrals. In both (n, n, p) and $(n, 0, p)$ tori, each unit cell has $4n$

atoms and thus the total number of atoms $N = 4np$. The $16np \times 16np$ Hamiltonian matrix can be written in a block form:

$$H = \begin{bmatrix} H_{1,1} & H_{1,2} & 0 & 0 & \cdots & 0 & H_{1,p} \\ H_{2,1} & H_{2,2} & H_{2,3} & 0 & \cdots & 0 & 0 \\ 0 & H_{3,2} & H_{3,3} & H_{3,4} & \cdots & 0 & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & 0 & \cdots & H_{p-1,p-2} & H_{p-1,p-1} & H_{p-1,p} \\ H_{p,1} & 0 & 0 & \cdots & 0 & H_{p,p-1} & H_{p,p} \end{bmatrix}, \tag{4}$$

with the $16n \times 16n$ matrix $H_{i,i}$ and $H_{i,j}$ representing the Hamiltonian of the ith unit cell and the interaction between the ith and the jth unit cells. Then the wavefunction can be written as

$$|\Psi\rangle = [\phi_1, \phi_2, \phi_3, \ldots, \phi_{p-1}, \phi_p]^{\mathrm{T}}, \tag{5}$$

with ϕ_j the wavefunction of the jth unit cell. The energy spectrum can be obtained by directly diagonalizing the Hamiltonian matrix. For the torus with a relatively large number of atoms, however, this is a time-consuming process or even impossible. To overcome this difficulty, we can make $H_{1,1} = H_{2,2} = \cdots = H_{p,p}$, $H_{1,2} = H_{2,3} = \cdots = H_{p-1,p} = H_{p,1}$, $H_{j,i} = H_{i,j}^{+}$, and $\phi_{j+1} = \mathrm{e}^{\mathrm{i}\varphi}\phi_j$ by using the rotational symmetry, with $\mathrm{e}^{\mathrm{i}\varphi}$ the phase factor, where $\varphi = j \times 2\pi/p$ ($j = 1, 2, \ldots, p$) is derived from the periodic boundary condition. The Schrödinger equation $H|\Psi\rangle = E|\Psi\rangle$ can be simplified as

$$[\mathrm{e}^{-\mathrm{i}\varphi} H_{1,2}^{+} + H_{1,1} + \mathrm{e}^{\mathrm{i}\varphi} H_{1,2}]\phi_1 = E\phi_1. \tag{6}$$

Now, the energy spectra for achiral type carbon nanotori can be calculated in a unified way only by solving equation (6) with $16n$ variables. Furthermore, this simplified calculation is readily extended to the case of chiral type carbon nanotori and similar systems with rotational symmetry such as polygonal nanotori [16]. We have validated this method through comparing the results for the small sized carbon nanotorus with those obtained from directly diagonalizing the total Hamiltonian.

By rearranging all the $4N$ eigenvalues in an increasing sequence, we can find the highest occupied molecular orbital (HOMO) energy and lowest unoccupied molecular orbital (LUMO) energy, corresponding to the $2N$th and the $(2N + 1)$th energy levels. The difference between the HOMO and LUMO energies is defined as the energy gap E_{g}. From the energy spectra, the average density of states (DOS) of each unit cell can be directly calculated using

$$\mathrm{DOS}(E) = \frac{1}{\pi p} \lim_{\delta \to 0^{+}} \sum_i \frac{\delta}{(E - \epsilon_i)^2 + \delta^2}, \tag{7}$$

with ϵ_i the ith eigenvalue. In our calculation, the adjustable width factor of the Lorentzian function δ is taken to be 0.005 eV.

3. Results and discussion

3.1. Curvature and hybridization effects

In this subsection, we mainly focus on the effects of curvature and hybridization, with no disorder introduced in the calculations.

Figure 1 illustrates the energy gap of the armchair type $(5, 5, p)$ nanotori as a function of the unit cell number p. The energy gap shows an oscillatory behaviour with increasing p. This oscillatory behaviour is similar to that of a finite length carbon nanotube [17], which arises from the changes in the bonding characteristics of the HOMO and LUMO orbitals with varying torus size. As p increases, the oscillation amplitude decreases, and the energy gap value converges
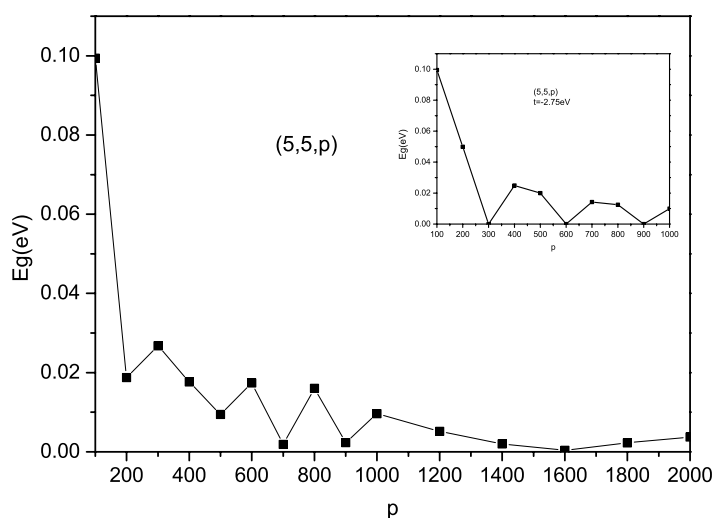
Figure 1. The energy gap versus p for the $(5, 5, p)$ torus. The inset shows the results obtained without considering the curvature and the hybridization effects.

slowly to zero. For a torus with a small radius ($p < 1000$), the energy gap can range from 2.339 to 99.413 meV, being that of a small gap semiconductor, while for relatively large p, the energy gap is generally very small, tending to zero. A semiconductor–metal phase transition may appear for some specific value of p, such as $E_g(p = 1600) = 0.407$ meV, while metallic behaviour can be expected for $(5, 5, p)$ in the case of sufficiently large p. Another thing worth noting is that the simple relation $E_g(p) = 0$ at $p = 3k$ (k an integer) does not apply in our four orbital TB calculation, unlike in the previous work [5, 6, 10]. This discrepancy can be ascribed to the curvature and hybridization effects, which are fully considered in our calculations but not in the latter. For clarity, we further calculate its electronic structure adopting the single π TB approximation, not including the curvature effects. As was expected, $E_g(p = 3k) = 0$ is well reproduced in the simple TB calculation, depicted in the inset of figure 1. The distinct difference generated by the two treatments indicates that the curvature and the hybridization effects should be considered in a more accurate calculation.

Also shown in figure 2 are the DOS of the armchair type nanotori at $p = 100, 300, 600, 800, 1600$. From figure 2, the spectrum of the $(5, 5, 100)$ torus with a relatively small torus radius exhibits a sequence of discrete quantum states, similar to those in previous work [10], just like the characteristic of the zero dimensional (0D) system (quantum dot). Interesting, the electron–hole asymmetry appears in the DOS spectra around the Fermi level. Similar behaviour was also observed for both small radius carbon nanotubes with large charge transfer, asymmetrically, away from the atom [12] and mechanically deformed multiwalled carbon nanotubes with a variety of topological defects [14]. In the case of the nanotorus, the local bond characteristic of the torus inner side differs from that of the torus outer side, which may lead to more complicated σ^*–π^* rehybridization due to high curvature [12–14], unlike that of the perfect nanotubes. This σ^*–π^* hybridization can affect the conduction electrons dramatically and hardly influence the valence electrons, which can lead to electron–hole asymmetry.

Another interesting observation is that the DOS of the $(5, 5, 800)$ torus with medium size exhibits not only well defined peaks but also the wavepacket-like (WPL) pattern. The DOS of different armchair carbon nanotori such as $(7, 7, p)$ and $(10, 10, p)$ tori are also calculated,
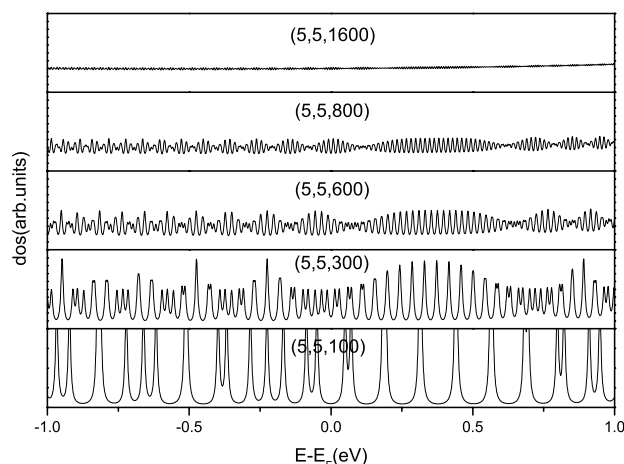
Figure 2. The dependence of DOS spectra on p for the $(5, 5, p)$ torus. From lower to upper planes, $p = 100, 300, 600, 800, 1600$ in sequence. Note that the DOS spectra have the same unit (states eV^{-1}/cell), corresponding to average contribution of each unit cell.

where the WPL feature is also found. This WPL pattern can be explained in terms of the nonuniform degeneracy caused by the specific interaction between atoms, related to the torus structure. With p increasing, both the well defined peaks and the WPL feature disappear, gradually. Therefore, one can expect the electronic structure to have the main characteristics of the quasi-one dimensional (1D) carbon nanotube for a sufficiently large carbon nanotorus. The DOS spectra of the nanotori evolve with increasing p from one characteristic of a 0D system to that of a quasi-1D system, which can be seen very clearly from figure 2.

To explore the dependence of the electronic properties on the torus type, we further calculate in figures 3–5 the energy gap and the DOS of the zigzag type of carbon nanotori. As can be seen from figure 3, the energy gap E_g of the $(6, 0, p)$ nanotori decreases rapidly with increasing p at smaller p ($p < 500$), while it almost keeps constant at larger p ($p > 1000$), approaching the band gap of about 0.11 eV for infinite $(6, 0)$ carbon nanotubes. The oscillatory characteristic presented by the armchair type, however, cannot be found in figure 3. Is there no energy gap oscillation in zigzag type carbon nanotori? We calculate in detail the energy gap of the $(6, 0, p)$ torus from $p = 800$ to 820. As a result, periodic oscillation is observed, with the period of two unit cells, as shown in figure 3, inset. It is shown that the oscillatory characteristic presents not only for the armchair type but also for the zigzag type nanotori, while the oscillatory period is absent for the armchair type tori. It is expected that a quasi-period oscillation may be obtained for a chiral type torus.

Figure 4 shows the DOS of the zigzag type $(6, 0, p)$ torus. No WPL feature is observed, unlike the case for the armchair type torus, while there appears similar asymmetrical behaviour. This is a general result for all zigzag type carbon nanotori. Our results show that the electronic properties of the nanotori depend to a high degree on both the torus diameter and the chirality of tube, which provides an experimental means for structure appraisal for the nanotorus devices.

Figure 5 presents the result for the typical semiconducting torus $(10, 0, p)$. The energy gap tends to increase with p, especially at smaller p ($p < 500$), in contrast to that for the $(6, 0, p)$ torus. This is mainly due to the fact that the modified low lying conduction band states are introduced into the band gap of this insulating nanostructure in the case of strong hybridization, leading its energy gap to be smaller [13]. When p is enough large, the energy
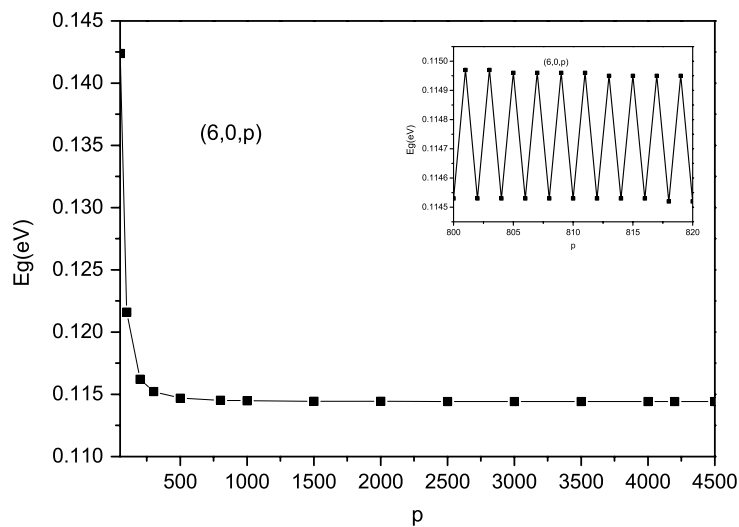
Figure 3. The energy gap of $(6, 0, p)$ torus as a function of p. The inset gives the energy gap from $p = 800$ up to $p = 820$.
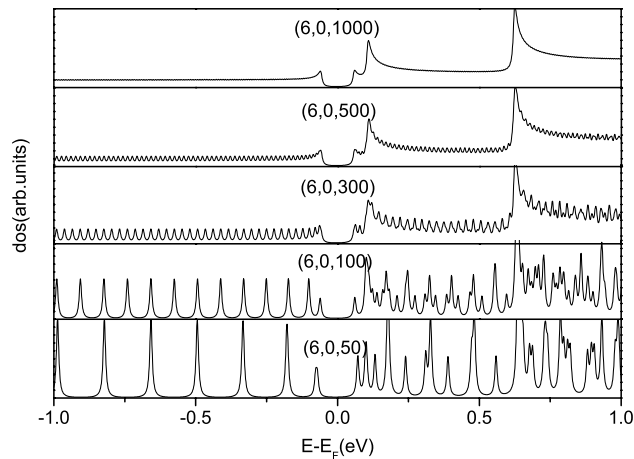

Figure 4. DOS plots of the $(6, 0, p)$ torus as a function of energy E for different p. From lower to upper planes, $p = 50, 100, 300, 500, 1000$ in sequence. Each spectrum corresponds to the average contribution of each unit cell.

gap hardly increases and approaches the limit of the infinite $(10, 0)$ nanotube, as in the case of the $(6, 0, p)$ torus.

3.2. Disorder effect

We now turn to exploring the disorder effect on the electronic structure of carbon nanotori. The disorder can be simulated by a random modulation of the on-site energies [5]. In order to preserve the rotational symmetry, the disorder is assumed to be distributed identically in each unit cell. Although this approximation is somewhat idealized compared with the realistic case, the results can give a qualitative description for the disorder effects. The range of the on-
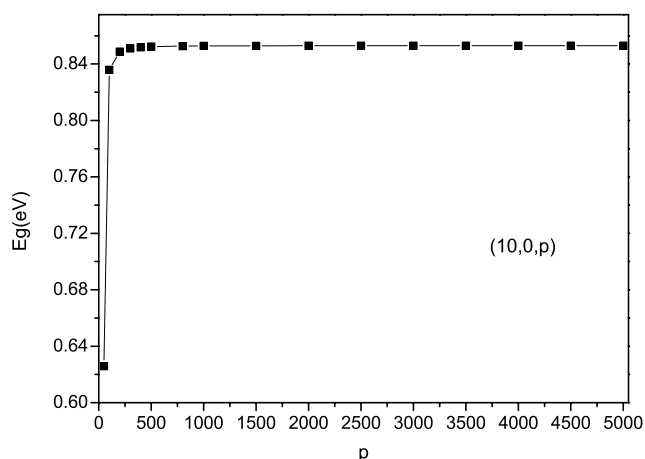
Figure 5. The energy gap of the $(10, 0, p)$ torus as a function of p.
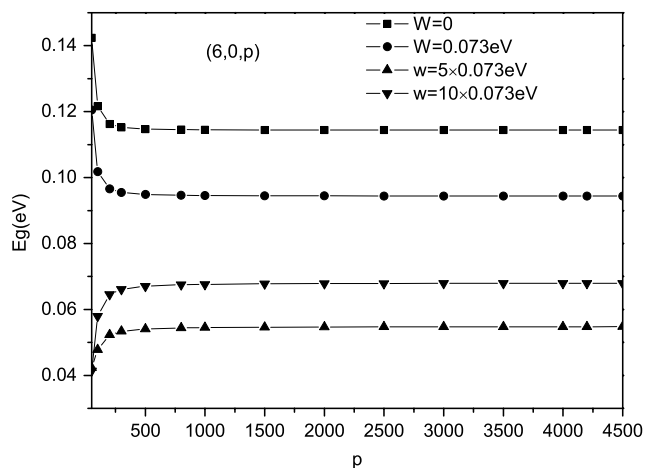
Figure 6. The energy gap of $(6, 0, p)$ torus as the function of p for different disorder strength.

site energy fluctuation is $[-W, W]$, with W the disorder strength. Four different W values are considered in our calculation, i.e., $W = 0 \times W_0, 1 \times W_0, 5 \times W_0, 10 \times W_0$, with $W_0 = 0.073$ eV. Taking the typical $(6, 0, p)$ torus, for instance, the calculated energy gaps are shown in figure 6. Compared with the case for $W = 0$, the energy gap is lowered by a constant amount at smaller W, such as $1 \times W_0$. This can be ascribed to the fact that new states induced by the disorder may be introduced into the energy gap, leading it to be smaller [18]. Interestingly, it is found that the energy gap at $W = 10 \times W_0$ is larger than that at $W = 5 \times W_0$. This means that for a given torus, there is a critical W_c above which the energy gap will become large with W. This can be understood from the fact that the disorder induced localization becomes more and more important. Therefore, one can expect that a semiconductor–insulator transition may appear at a strong enough disorder strength. In particular, it is shown that the variation tendency of the energy gap is dependent on the disorder strength. The energy gap decreases with p at smaller W, while it increases at relatively large W. This may be due to the competition between the structure and the disorder, both of which dominate the increase and/or decrease of the energy

gap with p. As for other types of carbon nanotori, the results are qualitatively unchanged, while they are at variance with those for the $(6, 0, p)$ torus owing to the different structures.

In the presence of disorder, the unit cell can be doubled and/or trebled in size in order to simulate a more realistic torus. The energy gap and DOS of the $(6, 0, p)$ torus were recalculated with the unit cell at double size and the results were similar to those obtained above. Additionally, relaxing the atoms on the torus can break the periodicity, which will substantially complicate the calculations. This will be considered in future work.

4. Summary

In summary, a reasonable and efficient method is developed for calculating the electronic structure of carbon nanotori by using the rotational symmetry. The dependences of the electronic structure on the torus size, the 'chirality', and the disorder are investigated. It is shown that the curvature and hybridization effects play very important roles in determining the electronic structure of this novel nanostructure. The energy gap exhibits different oscillatory characteristics depending on the structure of the tori. With increasing torus size, the electronic structures evolve from one characteristic of the 0D system to that of the quasi-1D system, and a semiconductor–metal phase transition has been observed. Also, the WPL feature in the DOS spectra is present for armchair type nanotori and absent for the zigzag type torus. The characteristic of energy gap oscillation presents not only for armchair type but also for zigzag type nanotori, while the oscillation period is absent for the former. These results provide an experimental means for structure appraisal of the nanotorus devices. Additionally, it is shown that the variation tendency of the energy gap is dependent on the disorder strength and the disorder induced semiconductor–insulator transition is expected at a strong enough disorder strength. The results have implications for our understanding of electronic properties and potential applications of carbon nanotori.

Acknowledgments

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