ORGANIC LETTERS

2007
Vol. 9, No. 21
4267−4270

Finite-Length Models of Carbon Nanotubes Based on Clar Sextet Theory

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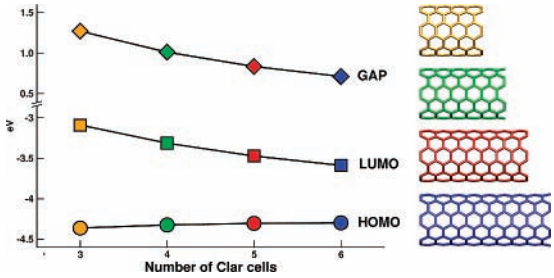
Received July 30, 2007

ABSTRACT



Finite-length models of metallic and semiconducting carbon nanotubes (CNTs) based on Clar sextet theory of aromatic systems are proposed. For metallic CNTs, the electronic properties of finite-length models converge monotonically to the values expected for quasi-monodimensional metallic systems. For semiconducting CNTs, the use of finite-length models as proposed in this work leads to a fast convergence of the electronic properties to the values expected for the corresponding infinite-length nanotube.

The development of technological applications based on carbon nanotubes (CNTs) often had to face intrinsic difficulties related to the accurate and unambiguous experimental determination of their properties, mostly due to the nonuniform and heterogeneous nature of the material at hand.[1] Consequently, in the past few years, an intense and active field of research on CNTs and their properties has been represented by computational modeling, which constitutes a favorable alternative to experimental techniques and, in many cases, a preferential investigation route.[2] Indeed, electronic structure methods allow accurate investigations on structural, reactive, and magnetic properties of nanostructured materials at an atomic level of detail. In particular, the largest part of electronic structure studies on this field has been carried out by applying density functional theory (DFT), which couples the possibility of dealing with nanosized model systems with reasonable computing demands. Therefore, most previous DFT calculations on CNTs and related systems were based on finite-length clusters or translationally repeated models constituted of up to a few hundreds of carbon atoms. However, it has been already shown that the particular choice of either cluster or periodic models of CNTs, including those considered in hybrid quantum mechanics/molecular mechanics (QM/MM)[3] techniques, could strongly bias the results of electronic structure calculations.[4,5] Indeed, both approaches could exhibit severe drawbacks. For example, the cluster and the periodic models could require a unit cell constituted of several hundreds of carbon atoms for the description of a chiral CNT.[6] Moreover, the use of finite-length cluster models, when applied through purely size-based criteria, provide contrasting result[7] and, as previ-

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10.1021/ol7018289 CCC: $37.00
Published on Web 09/14/2007

ously shown by Bettinger, slow convergence.[4] An alternative to this situation is given by the choice of model systems based on Clar sextet theory,[8] thus extending to CNTs many of the concepts widely applied to polycyclic aromatic hydrocarbons (PAHs), as pointed out by Randic in his outstanding review.[9] Thus, in analogy with PAHs, the bonding situation taking place in CNTs can be represented by a combination of two-electron π bonds and aromatic sextets (six-electrons π-conjugated circuits).[10] In particular, Ormsby and King demonstrated as the application of the Clar sextet theory provides a consistent (valence-bond like) representation of the bonding situation in CNTs, confirmed by the evaluation of nuclear independent chemical shifts[11] and hydrogenation energies.[12] Moreover, Matsuo et al. rationalized the inconsistencies observed for the electronic properties of finite-length (*n*,*n*) CNTs in terms of the different aromaticity of models used in calculations, in accordance with Clar theory.[13]

In this work, we apply a general formulation of Clar sextet theory to the definition of finite-length models of zigzag, armchair, and chiral CNTs. The advantages of using a finite-length Clar cell (FLCC) approach are manifold, in particular: (i) a consistent and uniform description of the electronic properties of different kinds of CNTs, often lacking in other finite-length models; (ii) fast and monotonic convergence of the electronic properties to the "bulk" (i.e., with an infinite number of carbon atoms) values; and (iii) remarkable computational benefits, due to the reduction, up to 1 order of magnitude, in the number of atoms employed in calculations, with respect to standard translationally repeated models.

To demonstrate the applicability of FLCC models, the energy of the highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), and corresponding HOMO−LUMO gap for a series of FLCC models of CNTs were analyzed. Indeed, the HOMO and LUMO energies, as well as the HOMO−LUMO gap, can be considered as good descriptors of many electronic properties of molecular systems, including reactivity.[14]

As previously suggested by Ormsby and King, the most convenient way to apply Clar theory to CNTs consists of defining the two-dimensional carbon atom network resulting from the unroll of the sidewall in terms of two translational basis vectors, which reflect the translational symmetry of a fully benzenoid graphene sheet.[11] This basis is connected to the conventional (*n*,*m*) CNT vector basis[15] by simple algebraic relationships and allows the Clar representation of the sidewall. Moreover, the Clar vector basis leads to a new definition of a primitive cell for the CNTs, which is usually smaller than the conventional (*n*,*m*) cell. From the primitive Clar cell, the infinite CNT is generated by application of a screw axis operation along the nanotube principal axis.[11] The definition of the sidewall topology in terms of the Clar cell basis leads to three different situations, depending on the value of the parameter *R*, defined as $R = \mathrm{mod}(n - m, 3)$.[11] For $R = 0$, the Clar cell is fully benzenoid and the corresponding infinite nanotube is metallic. In contrast, for $R = 1$ or $R = 2$, the Clar cell contains six-membered rings and a double bond (or two double bonds for (*n*, 0) CNTs with $R = 1$), and the corresponding CNTs are semiconducting. Following these considerations, we applied the same classification scheme to finite-length CNTs, generated by a finite number of applications of the screw axis operator to the Clar unit cell. In particular, we developed a set of models constituted of a finite number of replica (from 2 to 6) of the Clar unit cell along a screw axis parallel to the nanotube principal axis (see Figure 1). The dangling bonds at the edges of the model systems were saturated with hydrogen atoms. To demonstrate the consistency of the FLCC approach in general cases, several models of armchair, zigzag, and chiral CNTs, corresponding to different values of the parameter *R*, were taken into account (see Figure 1). The structures of

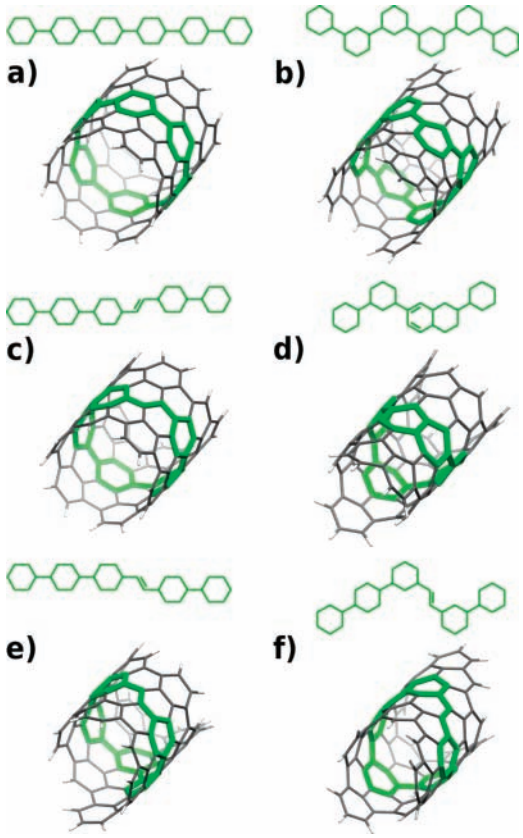

Figure 1. Optimized geometries of FLCC CNT models consisting of three unit cells used in calculations: (a) (6,6), (b) (9,0), (c) (6,5), (d) (7,0), (e) (6,4), and (f) (8,0) CNTs. The generating Clar cells and their corresponding planar representations are depicted in green.

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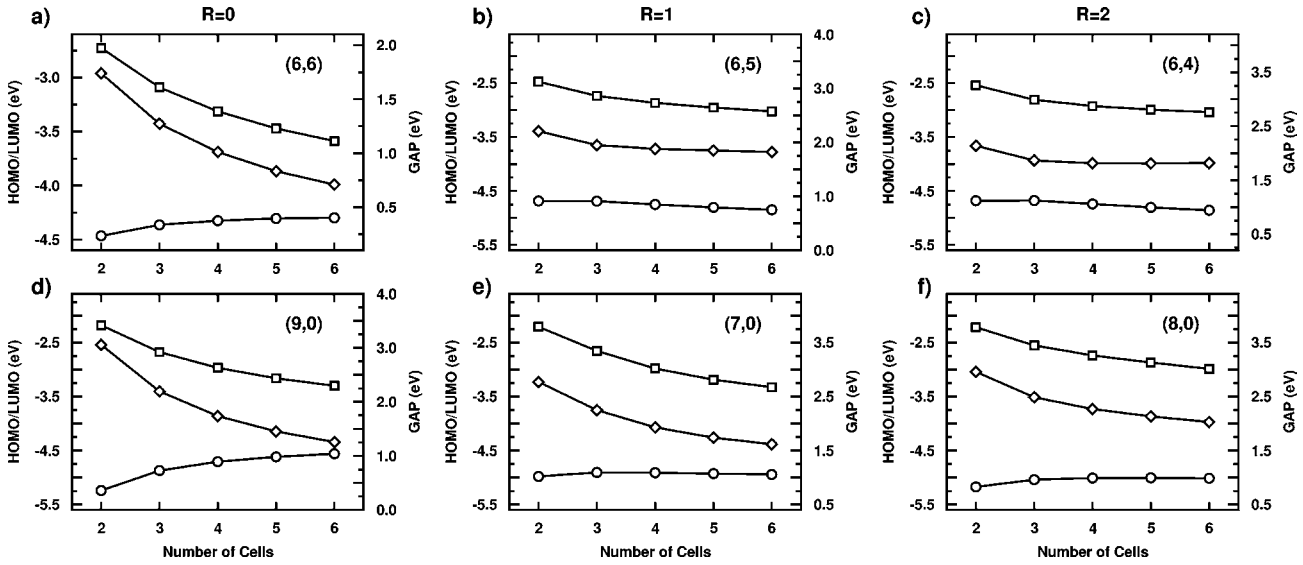

Figure 2. HOMO (circles) and LUMO (squares) energy levels (eV) and HOMO−LUMO gap (diamonds) for FLCC models of CNTs of different length as discussed as in the text: (a) (6,6), (b) (6,5), (c) (6,4), (d) (9,0), (e) (7,0), and (f) (8,0).

all systems under study were optimized at the B3LYP/3-21G level[16] as implemented in the Gaussian03 program package.[17] Orbital energies were evaluated at the same level of theory. The complete topology of Clar cells and FLCC models is given as Supporting Information. It is, however, worth noting that, in some cases, the Clar unit cells used throughout our work differ from their canonical representation, as for instance used in ref 11. Indeed, it is possible to choose different Clar unit cells, each of which generates the same CNT by application of the screw axis operator an infinite number of times. From this point of view, the choice of the Clar unit cell is somewhat arbitrary. Therefore, in our calculations the choice of a particular Clar unit cell was driven by an adequate description of the geometry of finite-length models, even for a small number of repeated cells. A comparison between canonical Clar unit cells and those used in our work is given as Supporting Information. The HOMO and LUMO energies and the HOMO/LUMO gaps for the FLCC models of Figure 1 and their dependence from the number of Clar cells are shown in Figure 2. The electronic properties of other FLCC models of different CNTs are shown as Supporting Information.

For models of (6,6) and (9,0) CNTs ($R = 0$, Figure 1a,b), the HOMO and LUMO energies exhibit a regular increase and decrease, respectively, with the nanotube size (see parts a and d of Figure 2). In particular, the LUMO energy decreases more rapidly than the increase in the HOMO energy, leading to an overall monotonic decrease of the HOMO−LUMO gap with the length of the model. These trends are consistent with the properties expected for finite-length models of metallic CNTs, where the band gap is zero at infinite nanotube length. Therefore, the use of Clar theory allows a consistent definition of the electronic properties of finite-length models for metallic CNTs, which can be particularly useful in the study of systems where a finite band gap is introduced, as for example in the case of doping or chemical reactions at the sidewall.

A different situation arises for semiconducting CNTs. As representatives of CNTs with $R = 1$, finite length models of (6,5) and (7,0) nanotubes (see parts c and d of Figure 1) were taken into account. The FLCC models of the (6,5) CNT exhibit a remarkable convergence of HOMO, LUMO, and HOMO−LUMO gap energies with the number of Clar cells, as shown in Figure 2b. The HOMO−LUMO gap converges to a value of 1.88 eV within a deviation of 0.06 eV already at a model length corresponding to 4 Clar unit cells (128 carbon atoms). Most notably, the use of a Clar unit cell drastically reduces the number of carbon atoms to take into account in calculations with respect to periodic or finite-length models based on the translational unit cell (364 C atoms for a (6,5) CNT). A similar trend can be observed for FLCC models of a (7,0) CNT (Figure 2e) where, on the other hand, a slightly slower convergence is noticed (0.12 eV within 5 Clar unit cells for the HOMO−LUMO gap).

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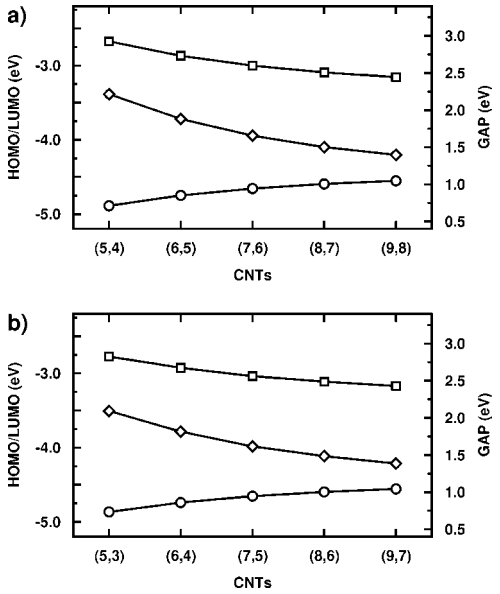

Figure 3. HOMO (circles), LUMO (squares) energy levels (eV) and HOMO−LUMO gap (diamonds) for FLCC models of CNTs of different diameters consisting of four unit cells: (a) $(n,n-1)$, $R = 1$, and (b) $(n,n-2)$, $R = 2$.

Analogous results were obtained for models of CNTs with $R = 2$. In this case, finite-length models of CNTs (6,4) and (8,0) nanotubes were considered (see Figure 1e,f). The convergence properties of HOMO, LUMO and gap for FLCC models of the (6,4) CNT (see Figure 2c) are remarkably similar to those obtained in the case of a (6,5) CNT. This is not surprising since the planar representations of Clar cells for (6,4) and (6,5) CNTs are mirror images of each other. Similar to the previous case, a slightly slower convergence is observed for FLCC models of the (8,0) CNT, where the HOMO−LUMO gap converges within a deviation of 0.10 eV for 5 Clar unit cells.

As a further assessment of the applicability of FLCC models to the theoretical study CNTs, the dependence of HOMO and LUMO energies and HOMO−LUMO gap with the diameter of chiral nanotubes ($R = 1$ and $R = 2$) was investigated. As shown in Figure 3, both in the case of $R = 1$ (Figure 3a) and $R = 2$ (Figure 3b), a regular and monotonic relationship between the observed properties and the CNT diameter is observed.

In summary, finite-length models of CNTs based on Clar sextet theory (FLCC) were proposed. The use of FLCC models provide a unified description of the electronic properties of CNTs. In particular, we have shown that the electronic properties of FLCC models for metallic CNTs, such as HOMO and LUMO energies and HOMO−LUMO gap, converge uniformly and monotonically to the values expected for quasi-unidimensional metallic systems. Moreover, FLCC models of semiconducting nanotubes exhibit a prompt convergence of HOMO and LUMO energies and HOMO−LUMO gap within a small number of carbon atoms. This results in remarkable computational advantages in using FLCC models with respect to finite-length or periodic models based on translationally repeated cells, especially for chiral CNTs. An accurate description of such properties is expected to play a crucial role in the consistent evaluation of the nanotube reactivity. Work is in progress to assess the applicability of FLCC models to the study of chemical reactions at the sidewall of CNTs.

Acknowledgment. This work was supported by MIUR (FIRB 2003: Molecular compounds and hybrid nanostructured materials with resonant and non resonant optical properties for photonic devices) and by the CNR (PROMO 2006). F.M. thanks Stefano Leoni (Max-Planck-Institut, Dresden) for fruitful discussions.

Supporting Information Available: FLCC planar models, electronic properties of models not discussed in the text, and optimized geometries of FLCC models at B3LYP/3-21g level of theory. This material is available free of charge via the Internet at http://pubs.acs.org.

OL7018289