

**First-principles calculations of the electronic structure of one-dimensional C<sub>60</sub> polymers**

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(Received 30 May 2005; revised manuscript received 22 August 2005; published 18 October 2005)

The geometrical and electronic properties of two dimers (one with  $C_{2h}$  symmetry) from the Stone-Wales rearrangement sequence of  $C_{60}$  dimers [described by E. Osawa and K. Honda, *Full Sci. Technol.* **4**, 939 (1996)] are investigated by density functional and tight-binding calculations. The trimer and the infinite periodic polymer derived from the  $C_{2h}$  symmetry dimer are shown to continue a decreasing trend of the energy gap between the highest occupied (HOMO) and the lowest unoccupied (LUMO) molecular orbitals to values smaller than 0.1 eV. The very small energy gap, in conjunction with the extension of the HOMO orbital over the whole cross-linkage region, provides an explanation for the observed conducting properties of electron beam irradiated  $C_{60}$  films.

DOI: [10.1103/PhysRevB.72.155416](https://doi.org/10.1103/PhysRevB.72.155416)

PACS number(s): 71.15.Mb, 71.20.Tx

**I. INTRODUCTION**

Several methods for producing  $C_{60}$  polymers have been reported.<sup>1,2</sup> In particular,  $C_{60}$  polymerization induced by light and electron-beam (EB) radiation is of great interest from a viewpoint of nanofabrication of  $C_{60}$ -based carbon materials and has been extensively investigated by Onoe *et al.* using *in situ* Fourier-transform infrared spectroscopy, *in situ* x-ray photoelectron spectroscopy, and *in situ* scanning tunneling microscopy.<sup>3-5</sup>

In EB polymerized films,  $C_{60}$  molecules have been experimentally found to coalesce to form tubular linkages.<sup>4,5</sup> Onoe *et al.*<sup>4</sup> have shown that the resistivity of a  $C_{60}$  film polymerized by EB irradiation amounts to 7  $\Omega$  cm, which is considerably smaller than that of solid  $C_{60}$  ( $10^8$ – $10^{14}$   $\Omega$  cm). The  $C_{60}$  polymer can be regarded as a  $\pi$ -electron conjugated system and its transition from insulator to conductor caused by EB irradiation is useful for developing carbon-based nanodevices.

Until recently, only a few theoretical studies on the structural and spectroscopic properties of peanut-shaped  $C_{60}$  dimers (viewed as possible building blocks of polymers) were available, relying essentially on semiempirical and tight-binding methods.<sup>5-7</sup> Density functional theory (DFT) calculations have been reported by Onoe *et al.*,<sup>8</sup> being carried out within the local density approximation (LDA) and using the frozen-core approximation. The main findings were that the highest occupied molecular orbital (HOMO) extends over the whole  $C_{60}$  dimer (without nodes in the cross-linkage region), the electrons being thus able to move freely without excitation in this extended  $\pi$ -conjugated system.

The recent first-principles studies by Tsukamoto and Nakayama<sup>9</sup> on isolated  $C_{60}$  dimers have investigated two types of stable tubular linkage structures (peanuts), referred to as P55 and P56. The calculations, based on pseudopotentials for the valence electron-carbon ion interactions and the LDA approximation for the exchange-correlation effects, show that the presence of eight-membered rings in the cross-linkage region of the P56 molecule (as compared to the P55 peanut) is accompanied by the decrease of the HOMO-LUMO energy gap (between the highest occupied and the

lowest unoccupied molecular orbitals) from 1.38 eV to 1.16 eV, but causes an increase of the total energy, making the P56 isomer less stable. More reliable electrical properties of a EB-polymerized  $C_{60}$  film have been investigated in terms of the electronic band structure of the one-dimensional bellows-shaped fullerene tubes originating in the P55 and P56 peanuts.<sup>10</sup> Band gaps of 1.13 and 1.28 eV, respectively, have been found (with reversed magnitudes relative to the respective peanuts), implying that both fullerene tubes have semiconducting properties. However, the connection between the original electronic structure of the  $C_{60}$  film and the metallic electrical properties induced by the EB irradiation is still not completely elucidated.

The main purpose of the present research is to provide all-electron DFT (density functional theory) electronic structure results, based on carefully assessed exchange-correlation functionals, for two  $C_{60}$  dimers and for more complex structures derived from these, with a view to elucidating the observed metallic behavior of EB-irradiated  $C_{60}$  films. However, tractable high-quality electronic structure calculations are currently limited to several tens of atoms and, consequently, investigations of larger molecules can be undertaken only if the symmetry properties can be efficiently exploited. From this perspective,  $C_{60}$  dimers showing symmetry are of considerable interest since they can be used as building blocks for nanotubes inheriting symmetry properties themselves.

Using the generalized Stone-Wales rearrangement, Osawa *et al.*<sup>11,12</sup> presented the sequence from the [2+2] dimer to the perfect  $C_{120}$  nanotube, involving 24 stable isomers. We investigated some of these isomers and, for further convenience, we designated the  $n$ th isomer in the pathway as  $P_n$ . The peanut-shaped isomer P4 showing  $C_{2h}$  symmetry, together with the trimer and the periodic nanotube derived from it, plays a central role in our calculations. In addition, we have considered the nonsymmetric peanut P12.

Since full DFT calculations for large carbon nanostructures without symmetry are out of reach of many powerful present-day computers, there is an obvious need for alternative approaches, involving less computational effort and preserving an acceptable level of accuracy. Tight-binding (TB)

schemes, extensively applied in the last two decades for the investigation of covalent systems, have proved to be valuable candidates. The TB parametrization employed in the present study is the elaborate and yet conveniently implementable scheme proposed by Papaconstantopoulos *et al.*,<sup>15</sup> which we have shown to describe accurately the structural and spectral properties of the  $C_{60}$  and  $C_{70}$  fullerenes, and of  $C_{36}$  oligomers.<sup>13,14</sup> The TB results compare fairly with those obtained with DFT and this validates the TB approach as a reliable alternative to be used in further calculations on large systems.

## II. CALCULATION METHODS

Throughout our DFT calculations we used the package GAUSSIAN 03.<sup>16</sup> We have performed all-electron optimizations for the determination of stable geometrical structures and self-consistent electronic ground states with the split valence polarized basis set 6-31 $G(d)$ , which has proved to yield reliable results at reasonable computation costs for medium-scale calculations.

In order to adopt an appropriate exchange-correlation functional, we compared in a first stage the electronic structure results obtained for the  $C_{60}$  fullerene with two recent functionals (conventionally named after their authors): the PBE exchange and, respectively, gradient-corrected correlation functionals of Perdew *et al.*,<sup>17</sup> and the HCTH exchange functional including gradient-corrected correlation of Hamprecht *et al.*<sup>18</sup> Both functionals reproduce well the experimental HOMO-LUMO gap of  $C_{60}$  (1.6–1.85 eV),<sup>19</sup> i.e., 1.668 eV for the PBE functional and 1.698 eV for the HCTH functional. Quite in contrast, the more popular functional B3LYP (Ref. 20) seems to perform rather poorly, yielding 2.762 eV, and we did not employ it in the actual calculations for polymers. The actual HOMO energies found for the PBE, HCTH, and B3LYP functionals have been  $-5.496$  eV,  $-5.600$  eV, and  $-5.987$  eV, respectively.

An additional test for the appropriateness of the PBE and HCTH functionals for describing  $C_{60}$  polymers regarded the comparison with the orbital energies yielded by the LSDA (local spin density approximation). Although this simple approximation is known to be useful for systems characterized by slowly varying charge densities, it is sometimes of comparable accuracy with more sophisticated exchange-correlation functionals incorporating long range gradient effects. However, whereas the HOMO-LUMO gap of  $C_{60}$  found by LSDA (1.674 eV) is still consistent with the PBE and HCTH values (despite the lowering of roughly 0.5 eV of both the HOMO and LUMO levels), the decrease of the energy gaps for the polymers with increasing size is found to be much too pronounced. For example, already the energy gaps of the dimer isomers appear to be more than 25% smaller than the PBE values, being lower even than the TB results. In addition, the geometrical structures found by LDA are significantly more compact.

The supplementary elasticity of the triple split valence basis 6-311 $G(d)$  and of the basis set 6-31+ $G(d)$  (including diffuse functions) did not appear to cause any significant differences in the results, yielding for  $C_{60}$  energy gaps of

1.656 eV and 1.650 eV, respectively, between slightly lowered HOMO and LUMO levels, and practically identical geometrical features. The increase in computational effort when using diffuse functions is, however, substantial due to the very slow SCF convergence for tight criteria, already the CPU time for the optimization of  $C_{60}$  increasing more than 30 times. This renders the envisaged computations of IR and Raman spectra for the optimized polymers virtually unfeasible with basis sets including diffuse functions.

In order to achieve convergence in the DFT runs, especially in the case of the periodic  $C_{60}$  polymer, the usage of tight convergence criteria and an ultrafine integration grid for the evaluation of the exchange-correlation functional turned out to be essential. Even by optimally exploiting the polymer symmetry, for the periodic polymer convergence can only be achieved in roughly a couple of weeks with up-to-date single-processor computers (Pentium 4 at 3 GHz and Alpha EV68 at 1 GHz).

The TB approaches can be viewed as simplified two-center-oriented *ab initio* methods, with the electronic properties calculated from a parametrized representation of the Kohn-Sham equation. In the TB parametrization of Papaconstantopoulos *et al.*,<sup>15</sup> validated here as a counterpart to DFT with a view to calculations which are otherwise not tractable, the total energy is expressed as a sum of one-electron energies,  $\epsilon_k$ , which are the eigenvalues of a parametrized representation of the Kohn-Sham equation. The Hamiltonian  $\mathbf{H}$  and the overlap matrix  $\mathbf{S}$  are expressed relative to a nonorthogonal set of atom-centered orbitals. The forces acting on the atoms can be expressed analytically and this is an essential aspect in our geometry optimizations, which have been carried out by simulated annealing embedded in molecular dynamics (MD).<sup>13,14</sup>

## III. RESULTS AND DISCUSSION

Among the  $C_{60}$  polymers investigated in this study, three have been chosen to have well-defined ( $C_{2h}$ ) symmetry: the P4 peanut described by Osawa *et al.*<sup>11</sup> (denoted simply by  $C_{120}$  in what follows), the trimer derived from P4 (denoted by  $C_{180}$ ), and the corresponding infinite periodic bellows-shaped polymer. The fourth polymer considered was the P12 peanut, chosen as a representative for the nonsymmetric intermediate structures of the Stone-Wales rearrangement sequence leading to the perfect nanotube.

Some of the relevant electronic and geometrical properties of the investigated  $C_{2h}$  symmetry polymers are listed in Table I, along with the reference results for the  $C_{60}$  fullerene, which provided the benchmark problem to validate the employed methods. The DFT results obtained with the PBE and HCTH exchange-correlation functionals are presented comparatively with the those yielded by the TB calculations. In particular, the geometrical features obtained with the three methods can be seen to agree for each polymer species. The translation vector for the periodic polymer is found to be little different from the intercage distances of the dimer and the  $C_{180}$  trimer. The transverse cage extents,  $d_1$  and  $d_2$ , of the three  $C_{2h}$  symmetry polymers are similar for PBE, HCTH, and TB, as well. The HOMO-LUMO gaps, which are known

TABLE I. HOMO-LUMO (band) gap  $\Delta$  and geometrical features of the  $C_{60}$  fullerene and its  $C_{2h}$  symmetry polymers. For  $C_{60}$ ,  $D$  is the cage extent, and  $d_1$  and  $d_2$  are the minimum and maximum bond lengths, respectively. For the dimer and trimer,  $D$  is the intercage distance, while for the periodic polymer it represents the length of the translation vector. For the dimer, trimer, and the periodic polymer,  $d_1$  and  $d_2$  are transverse extents.

	Functional	$\Delta$ (eV)	$D$ (Å)	$d_1$ (Å)	$d_2$ (Å)
$C_{60}$	PBE	1.668	6.987	1.405	1.457
	HCTH	1.698	6.945	1.397	1.448
	TB	1.711	6.959	1.411	1.445
$C_{120}$	PBE	0.333	9.004	6.965	6.912
	HCTH	0.388	8.970	6.919	6.877
	TB	0.294	8.962	6.934	6.886
$C_{180}$	PBE	0.107	9.013	6.965	6.913
	HCTH	0.168	8.978	6.919	6.878
	TB	0.050	8.987	6.932	6.886
$C_{60}$ polymer	PBE	0.021	8.964	7.036	6.750
	HCTH	0.083	8.935	6.962	6.734

to be sensitive calculation parameters, are consistent in the case of  $C_{60}$  and  $C_{120}$  for all three methods, while the small gap values for  $C_{180}$  and the periodic polymer are rather scattered. This behavior of the relative gap differences is not totally surprising, having in view the monotonous decrease of the HOMO-LUMO gap with increasing polymer size, which suggests a gradual transition from an insulating to a conducting character.

The optimized geometrical structure of the  $C_{2h}$  symmetry dimer and the corresponding HOMO orbital obtained with the PBE functional are depicted in Fig. 1 (the differences by using the HCTH functional are not significant). As one may easily notice, the intercage linkage is realized by four atoms originating from the two facing pairs of hexagons of the initial  $C_{60}$  cages. The Mulliken charges assigned to the atoms span a narrow interval, in the case of the PBE functional between  $-0.030e$  (light red) and  $+0.055e$  (light green). The HOMO and LUMO energies obtained with the PBE (HCTH) functional amount to, respectively,  $E_{\text{HOMO}} = -0.180$  ( $-0.184$ ) a.u. and  $E_{\text{LUMO}} = -0.168$  ( $-0.170$ ) a.u. The HOMO orbital appears to extend over the whole waist region, bridging the two cages. The extended HOMO-orbital combined with the reduced HOMO-LUMO gap (0.333 eV for PBE) as compared to the  $C_{60}$  value (1.668 eV), corroborates the incipient metallic behavior of the P4 peanut. The electron densities in the cap regions appear, on the contrary, to be quite modest. It is worth mentioning that the calculated HOMO-LUMO gap (around 0.3 eV for all methods) is significantly lower than the results obtained by Tsukamoto and Nakayama<sup>9</sup> for the peanuts P55 (1.38 eV) and P56 (1.16 eV). We ascribe this qualitative discrepancy to the more appropriate exchange-correlation functionals used in the present study, which turned out to have a crucial influence.

The  $C_{2h}$  symmetry trimer based on the P4 peanut is shown in Fig. 2. The HOMO and LUMO energies obtained

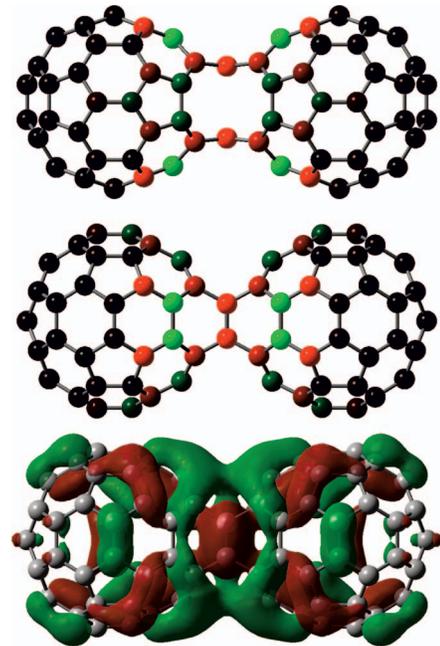


FIG. 1. (Color) Geometrical structure (the upper views are rotated longitudinally by  $90^\circ$ ), Mulliken charges, and HOMO orbital (isovalue 0.01) of the  $C_{2h}$  symmetry  $C_{60}$  dimer (P4).

with the PBE (HCTH) functional are, respectively,  $E_{\text{HOMO}} = -0.175$  ( $-0.179$ ) a.u. and  $E_{\text{LUMO}} = -0.171$  ( $-0.173$ ) a.u. The spatial distribution of the Mulliken charges in the two waist regions and the spanned interval (between  $-0.030e$  and  $+0.056e$  for the PBE functional) are similar to those of the dimer. The HOMO orbital in the two cross-linkage regions, too, shows qualitatively the same behavior, bridging the cages. However, a new feature emerges, i.e. a transverse nodal plane through the middle of the central cage, which appears to limit the delocalization of the electrons to the waist regions. It should be noted that for all methods, the HOMO-LUMO gap of the trimer is significantly reduced as compared to the dimer, continuing the monotonous decrease with respect to the  $C_{60}$  monomer.

The  $C_{2h}$  symmetry linear periodic  $C_{60}$  polymer based on the P4 peanut is depicted in Fig. 3. We have chosen to replicate the structure relative to transverse cross sections pass-

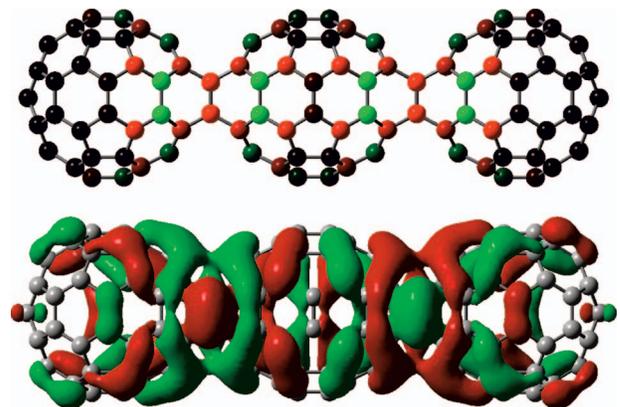


FIG. 2. (Color) Geometrical structure and HOMO orbital (isovalue 0.01) of the  $C_{2h}$  symmetry  $C_{60}$  trimer based on the P4 peanut.

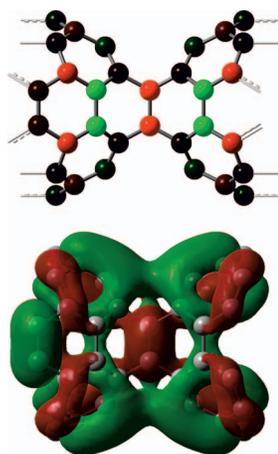


FIG. 3. (Color) Geometrical structure and highest occupied orbital (isovalue 0.01) of the  $C_{2h}$  symmetry linear periodic  $C_{60}$  polymer based on the P4 peanut. The Mulliken charges are situated between  $-0.044e$  (light red) and  $+0.059e$  (light green) for the PBE functional.

ing through neighboring cage centers, in order to perturb as little as possible the cross-linkage region, where the highest HOMO/LUMO electron densities have been found for  $C_{120}$  and  $C_{180}$  and where they were also expected to occur for the periodic polymer. The energies of the highest occupied and the lowest unoccupied electron states obtained with the PBE (HCTH) functional are, respectively,  $E_{\text{occ}} = -0.182$  ( $-0.186$ ) a.u. and  $E_{\text{virt}} = -0.181$  ( $-0.183$ ) a.u. As one may easily notice from Fig. 3, the highest occupied orbital is quite similar to the HOMO orbital of the dimer in the cross-linkage region. It is also interesting to notice that the energy of the highest occupied electron state is closer to the dimer result than to the one for the trimer, in which the central cage slightly perturbs the symmetry of the orbital in the waist regions. The very narrow band gap (under 0.1 eV) is an order of magnitude lower than the band gaps calculated by Tsukamoto and Nakayama<sup>9,10</sup> for the peanuts P55 and P56, and, in conjunction with the notable extension of the highest occupied orbital, it supports the explanation of the observed metallic behavior of the EB-irradiated  $C_{60}$  films. The separation of the Mulliken charges can be seen to be slightly larger than for the dimer and trimer.

The optimized P12 peanut obtained by using the PBE exchange-correlation functional is shown in Fig. 4, together with its HOMO orbital, and is meant to provide an example of dimer without symmetry properties, in the middle of the Stone-Wales rearrangement sequence.<sup>11</sup> The calculated HOMO and LUMO energies are, respectively,  $E_{\text{HOMO}} = -0.164$  a.u. and  $E_{\text{LUMO}} = -0.152$  a.u., leading to a HOMO-LUMO gap of 0.309 eV, very close to the one obtained for the symmetrical P4 peanut (see Table I). The HOMO orbital of the P12 dimer encompasses the whole structure and sug-

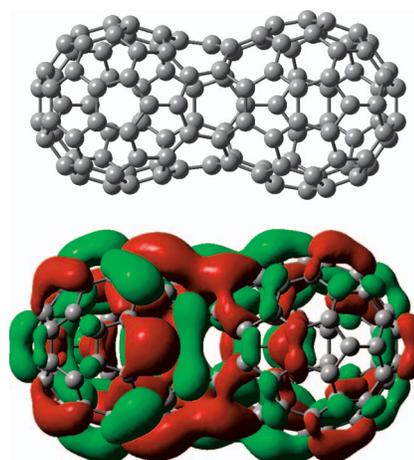


FIG. 4. (Color) Geometrical structure and HOMO orbital (isovalue 0.01) of the P12 peanut.

gests even more delocalized electrons than in the case of P4. In conjunction with the low HOMO-LUMO gap, this again supports the explanation of the transition from insulator to conductor observed for EB-irradiated  $C_{60}$  films.

#### IV. CONCLUSIONS

The electronic and geometrical properties of the  $C_{60}$  fullerene and its polymers obtained with the PBE and HCTH exchange-correlation functionals, proved to provide an appropriate description of  $C_{60}$  polymers, are consistent with the TB results, and reconfirmed the appropriateness of TB calculations for large carbon structures.

The investigated linear polymers show HOMO orbitals which extend over the cross-linkage region between adjacent  $C_{60}$  cages, the electrons being thus able to move freely without excitation in these extended  $\pi$ -conjugated systems. The HOMO-LUMO gaps are significantly lower than the hitherto published results ( $<0.4$  eV) and decrease with increasing polymer size (number of coalesced  $C_{60}$  cages) towards the value for the infinite polymer.

The small HOMO-LUMO gaps do not appear to depend significantly on the structure of the cross-linkage region, but rather on the polymer size and they would allow for transitions caused by small (thermal) excitations, supporting the observed metallic character of the electron-beam irradiated  $C_{60}$  films. The maximum electron charge concentration occurs at the atoms engaged in the transverse double bonds in the cross-linkage region.

#### ACKNOWLEDGMENTS

One of the authors (T.A.B.) gratefully acknowledges a visiting professor position at the Tokyo Institute of Technology.

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