

Electronic structure calculations of peanut-shaped C₆₀ polymers

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The geometrical and electronic properties of a C₆₀ dimer (having C_{2h} symmetry) are investigated by density functional and tight-binding calculations. The energy gap between the highest occupied and the lowest unoccupied (molecular) orbitals for the trimer and the infinite periodic polymer derived from the considered dimer continue a decreasing trend to values smaller than 0.1 eV. The very small energy gap and the extension of the highest occupied orbital provide an explanation for the observed conducting properties of electron beam irradiated C₆₀ films.

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1. Introduction

The initial report on the C₆₀ photopolymerization [1] was followed by numerous publications dealing with methods to produce C₆₀ polymers [2]. Polymerization induced by light and electron-beam (EB) irradiation, in particular, is of great interest for the nanofabrication of C₆₀-based carbon materials. The latter method was extensively investigated by Onoe et al. by in situ Fourier-Transform infrared spectroscopy, in situ X-ray photoelectron spectroscopy, and in situ scanning tunnelling microscopy [3-5]. The resistivity of an EB irradiated C₆₀ film was found to amount to 7 Ω·cm, which is considerably smaller than the value for solid C₆₀ (10⁸-10¹⁴ Ω·cm).

Only few theoretical studies on the structural and spectroscopic properties of peanut-shaped C₆₀ dimers (as possible building blocks for polymers) are available, being essentially based on semi-empirical and tight-binding methods [5-7]. Density functional theory (DFT) calculations have been reported initially by Onoe et al. [8] and were carried out within the local density approximation (LDA) by using the frozen-core approximation. The recent first-principles studies of Tsukamoto and Nakayama [9] on isolated C₆₀ dimers have investigated two types of stable tubular linkage structures (peanuts), referred to as P55 and P56. The calculations, based on pseudo-potentials for the valence electron-carbon ion interactions and the LDA approximation for the exchange-correlation effects have yielded HOMO-LUMO energy gaps (between the highest occupied and the lowest unoccupied molecular orbitals) of 1.38 eV and 1.16 eV, respectively. More reliable electrical properties of a EB-polymerized C₆₀ 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 [10]. Band gaps of 1.13 and 1.28 eV, respectively, have been found (just with reversed magnitudes relative to the respective peanuts), implying that both fullerene tubes have semiconducting properties.

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 C₆₀ dimers and for more complex structures derived from these, with a view to elucidating the observed metallic behaviour of EB irradiated C₆₀ 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 provided symmetry properties can be efficiently exploited.

Using the generalized Stone-Wales rearrangement, Osawa et al. [11,12] have presented the sequence from the [2+2] dimer to the perfect C₁₂₀ nanotube, involving 24 stable isomers. We have investigated some of these isomers and, for further convenience, we designate 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, play the central role in our calculations.

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

parameterization employed in the present study is the efficient scheme proposed by Papaconstantopoulos et al. [13], 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 [14,15]. 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.

2. Calculation methods

The DFT calculations reported in this paper have been carried out with the package Gaussian 03 [16]. 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 6-31g(d), which has proved to yield reliable results at reasonable computation costs.

With the aim of adopting the most appropriate exchange-correlation functional, we have compared in a first stage the electronic structures of C_{60} obtained with two recent functionals: the PBE exchange and PBE gradient-corrected correlation functionals of Perdew et al. [17], and the HCTH exchange functional including gradient-corrected correlation of Hamprecht et al. [18]. Both functionals reproduce very well the experimental HOMO-LUMO gap of C_{60} (1.6-1.85 eV.) [19], i.e. 1.668 eV for the PBE functional and 1.698 eV for the HCTH functional. Quite on the contrary, the popular B3LYP functional [20] seems to perform rather poorly, yielding 2.762 eV, and we did not employ it furthermore.

Tight-binding (TB) approaches can be viewed as simplified two-centre-oriented *ab initio* methods, with the electronic properties calculated from a parameterized representation of the Kohn-Sham equation. In the TB parameterization of Papaconstantopoulos et al. [13], validated here as efficient 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, which are the eigenvalues of a parameterized representation of the Kohn-Sham equation. The Hamiltonian and the overlap matrix are expressed relative to some non-orthogonal 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) [14,15].

3. Results and discussion

The three C_{60} polymers investigated in this study have been chosen to have well-defined (C_{2h}) symmetry: the P4 peanut described by Osawa et al. [11] (denoted simply by C_{120} in what follows), the derived trimer (denoted by C_{180}), and the corresponding infinite periodic polymer.

Some relevant electronic and geometrical properties of the investigated C_{2h} symmetry polymers are listed in

Table 1. 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 agree for each polymer species. The translation vector for the periodic polymer is found to be very little different from the inter-cage 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 to be sensitive calculation parameters, are consistent in the case of C_{60} and C_{180} for all three methods, while the small gap values for C_{180} and the periodic polymer are rather scattered. We note the monotonous decrease of the HOMO-LUMO gap with increasing polymer size, suggesting a gradual transition from an insulating to a conducting character.

Table 1. HOMO-LUMO (band) gap Δ and geometrical features of the C_{60} fullerene and its C_{2h} symmetry polymers. For C_{60} , D is the cage extent, 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	Δ [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

The equilibrium structure of the C_{2h} symmetry dimer and its HOMO-orbital obtained with the PBE functional are depicted in

Fig. 1 (the differences in the HCTH results are minor). The inter-cage linkage is formed by four atoms from the facing hexagons of the C_{60} cages. The Mulliken charges assigned to the atoms lie 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 are respectively $E_{\text{HOMO}} = -0.180$ (-0.184) a.u. and $E_{\text{LUMO}} = -0.168$ (-0.170) a.u. The HOMO-orbital extends over the whole waist region and its notable extent 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 behaviour of the P4 peanut. The electron densities in the cap regions appear to be rather small. It is noteworthy that the HOMO-LUMO gap (around 0.3 eV for all methods) is significantly lower than the values reported by Tsukamoto and Nakayama [9] for the peanuts P55 (1.38 eV) and P56 (1.16 eV), and we ascribe the disagreement to the more appropriate exchange-correlation functionals used here.

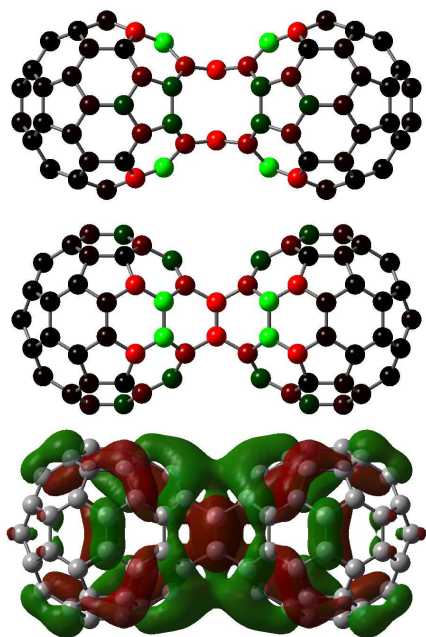


Fig. 1. Geometrical structure (the upper views are rotated longitudinally by 90°), Mulliken charges, and HOMO-orbital (isovalue 0.01) of the C_{2h} symmetry C_{60} dimer (P4).

The C_{2h} symmetry trimer based on the P4 peanut is shown in Fig. 2. The HOMO and LUMO energies obtained 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 distribution of the Mulliken charges in the two waist regions are similar to those of the dimer (between $-0.030e$ and $+0.056e$ for the PBE functional). The HOMO-orbital, too, shows qualitatively the same behavior, bridging the cages. However, a new feature appears - a transverse nodal plane through the middle of the central cage, which seems to limit the delocalization of the electrons. Anyway, 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.

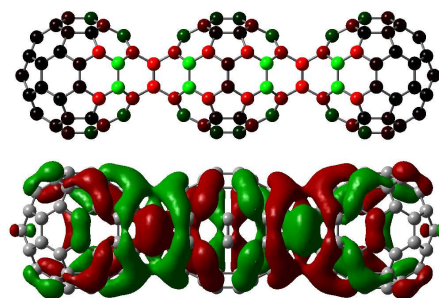


Fig. 2. Geometrical structure and HOMO-orbital (isovalue 0.01) of the C_{2h} symmetry C_{60} trimer based on the P4 peanut.

The C_{2h} symmetry linear periodic C_{60} polymer based on the P4 peanut is shown in Fig. 3. 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 [10] 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 behaviour of the EB irradiated C_{60} films. The separation of the Mulliken charges is slightly larger than for the dimer and trimer.

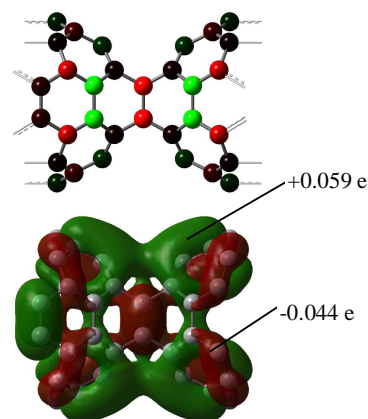


Fig. 3. Geometrical structure and highest occupied orbital (isovalue 0.01) of the C_{2h} symmetry linear periodic C_{60} polymer based on the P4 peanut. The Mulliken charges are situated between $-0.044e$ and $+0.059e$ for the PBE functional.

4. Conclusions

The electronic and geometrical properties of the C₆₀ fullerene and its polymers obtained with the PBE and HCTH exchange-correlation functionals, proved to provide an appropriate description of C₆₀ polymers, are consistent with the TB results, reconfirming 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 C₆₀ cages, the electrons being thus able to move freely in these extended π -conjugated systems. The HOMO-LUMO gaps are significantly lower than the hitherto published results (< 0.4 eV) and decrease with increasing polymer size 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 C₆₀ films. The maximum electron charge concentration occurs at the atoms engaged in the transverse double bonds in the cross-linkage region.

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