

# A Theoretical Study of Closed Polyacene Structures

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## Abstract

*The aim of this work is to study the electronic properties of three different groups of graphene nanostructures using modern Quantum Chemistry methods. The importance lies in the fact that these results could help to understand the electric and magnetic behavior of graphenes of finite-size involved herein.*

## Introduction

Graphene is the name given to a flat monolayer of carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice, and is a basic building block for graphitic materials of all other dimensionality[1]. We will study three different groups of graphene nano islands (GNI):

- Hexagons (H\_L)
- Rhombuses (R\_L)
- Triangles (T\_L)

It is worthy to point out, that we will focus in finite graphene sheets. Each group of GNI will be composed of two structures of different sizes. We are interested in the electronic properties[2,3] of them (such as localizability), as well as finite-size effects, and magnetic properties.

## Computational Details

All geometries were optimized at RHF level. The final bond distances and bond angles are very close to the ideal values (120° for the angles, 1.38Å and 1.08Å for the C-C and C-H bonds, respectively). The orbitals were calculated at RHF, and CAS-SCF level. The dynamical electronic correlation was recovered using Multireference perturbation theory. The systems were studied with a minimal and an ANO contracted basis set of Roos using the Quantum Chemistry Software MOLPRO. The level of theory employed was:

- CAS-SCF (Complete Active Space Self Consistent Field).
- NEVPT2 (n-Electron Valence Perturbation Theory).

## References

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- [3] M. Bendikov, H.M. Duong, K. Starkey, K.N. Houk, E.A. Carter, and F. Wudl, J. Am. Chem. Soc., 126, 7416, (2004).

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## Results

### Hexagons

**Table 1: Relative energies ( $\Delta E$ ) for the different spin states of hexagonal polyacenes, in kJ/mol.**

| State      | H_3      |         |         |         |         |         | H_4    |        |        |        |
|------------|----------|---------|---------|---------|---------|---------|--------|--------|--------|--------|
|            | STO-3G   |         | VDZ     |         | VDZP    |         | STO-3G |        | VDZ    |        |
|            | CAS-CI   | NEVPT2  | CAS-CI  | NEVPT2  | CAS-CI  | NEVPT2  | CAS-CI | NEVPT2 | CAS-CI | NEVPT2 |
| $^1A_{1g}$ | 0.000    | 0.000   | 0.000   | 0.000   | 0.000   | 0.000   | 0.000  | 0.000  | 0.000  | 0.000  |
| $^5A_{1g}$ | 1210.122 | 704.043 | 975.553 | 520.126 | 964.750 | 436.420 | 36.949 | 15.634 | 38.118 | 6.873  |

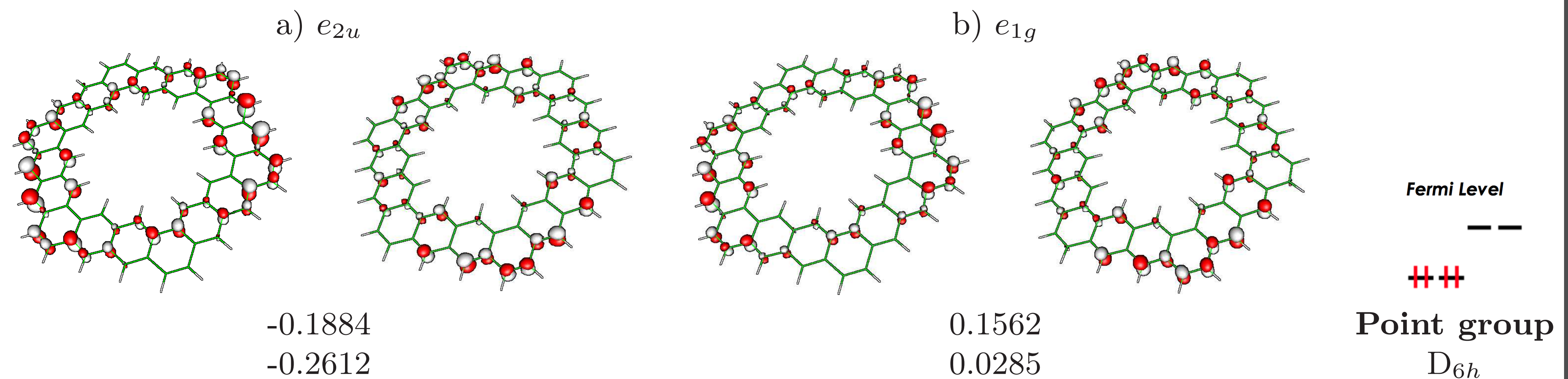


Figure 1. Frontier orbitals for the hexagonal polyacene H\_4: the two degenerate  $e_{2u}$  HOMO's, and  $e_{1g}$  LUMO's are shown.

### Rhombuses

**Table 2: Relative energies ( $\Delta E$ ) for the different spin states of rhombus polyacenes in kJ/mol.**

| State   | R_4    |        |        |        |        |        | R_5    |        |        |        |
|---------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
|         | STO-3G |        | VDZ    |        | VDZP   |        | STO-3G |        | VDZ    |        |
|         | CAS-CI | NEVPT2 | CAS-CI | NEVPT2 | CAS-CI | NEVPT2 | CAS-CI | NEVPT2 | CAS-CI | NEVPT2 |
| $^1A_1$ | 0.000  | 0.000  | 0.000  | 0.000  | 0.000  | 0.000  | 0.000  | 0.000  | 0.000  | 0.000  |
| $^3B_2$ | 1.653  | 2.401  | 4.550  | 6.580  | 4.236  | 6.433  | 0.157  | 0.379  | 0.668  | 1.900  |

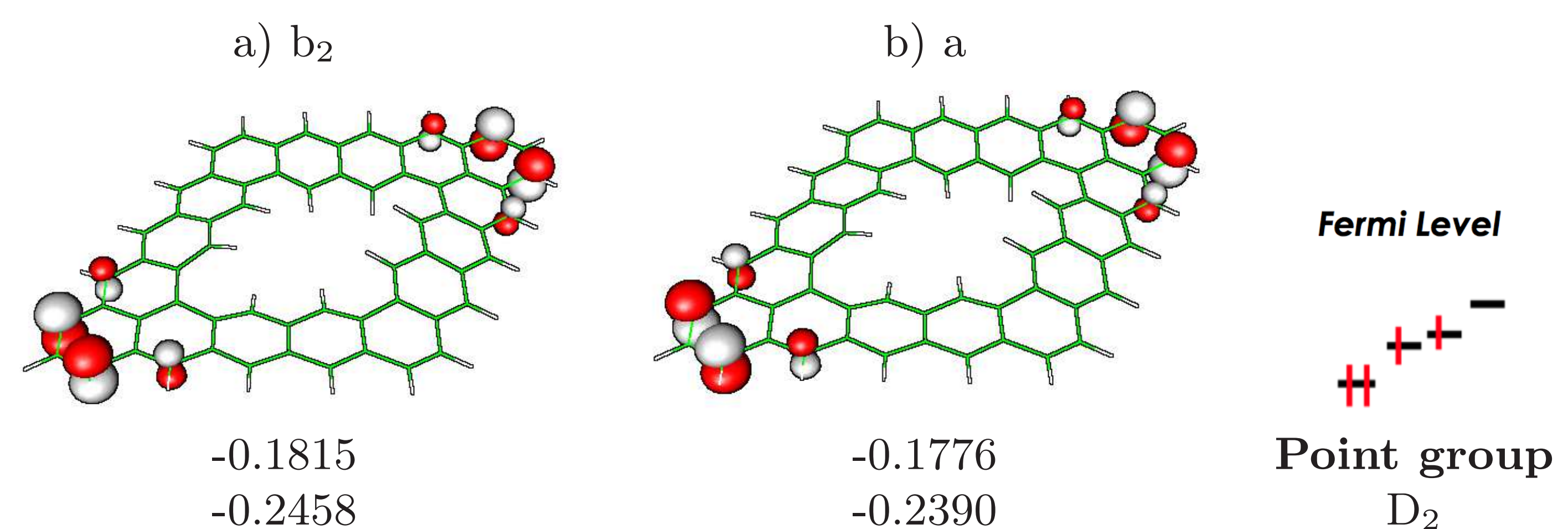


Figure 2: Active orbitals for the rhombus polyacene R\_5, having a and  $b_2$  symmetry.

### Triangles

**Table 3: Relative energies ( $\Delta E$ ) for the different spin states of triangular polyacenes in kJ/mol.**

| State   | T_6    |        |        |        |        |        | T_7    |        |        |        |
|---------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
|         | STO-3G |        | VDZ    |        | VDZP   |        | STO-3G |        | VDZ    |        |
|         | CAS-CI | NEVPT2 | CAS-CI | NEVPT2 | CAS-CI | NEVPT2 | CAS-CI | NEVPT2 | CAS-CI | NEVPT2 |
| $^4A_1$ | 0.000  | 0.000  | 0.000  | 0.000  | 0.000  | 0.000  | 0.000  | 0.000  | 0.000  | 0.000  |
| $^2E$   | 0.871  | 1.301  | 2.317  | 2.429  | 1.673  | 1.640  | 0.233  | 0.417  | 0.702  | 0.702  |

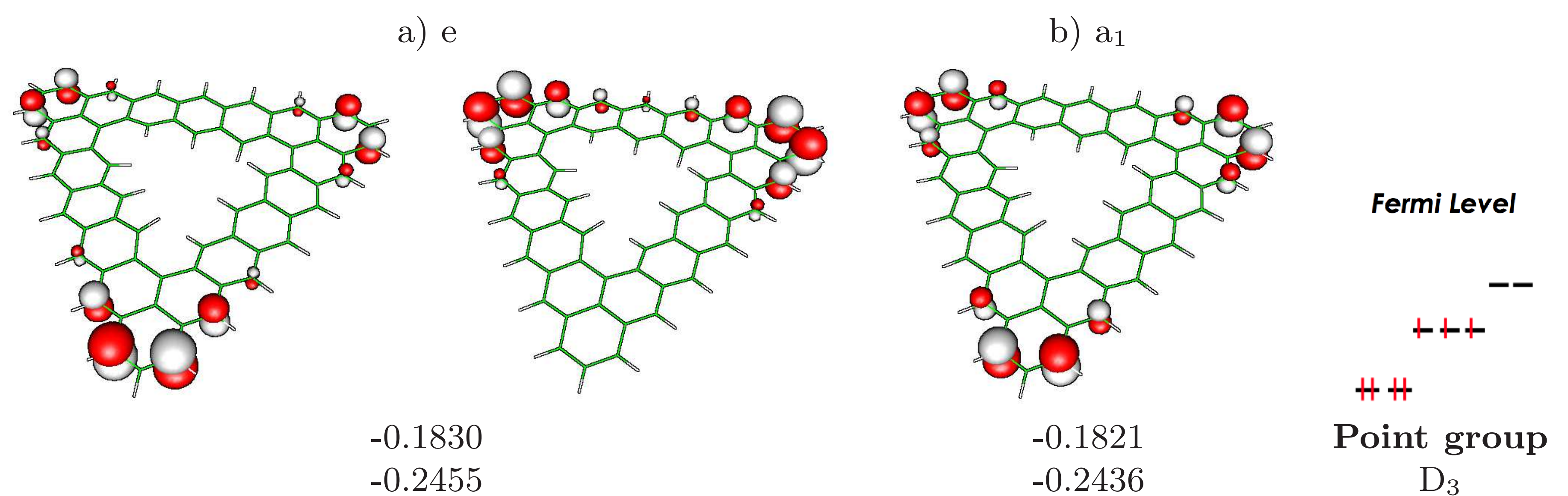


Figure 3: The three active orbitals for the triangular polyacene T\_7, having  $e$  and  $a_1$  symmetry.

## Conclusions

- Frontier orbitals are localized at the border of the structures, confirming the edge effects.
- The orbital-energy spectra obtained at tight-binding level was invariably, and the Ovchinnikov rule was systematically fulfilled.
- T\_L are gapless (there are degenerated orbitals at their Fermi level). Its ground state is a quartet.
- H\_L is a singlet in its ground state. The gap between HOMO, and LUMO tends to decrease when the size of the GNI increases (metallicity behavior).
- R\_L are more stable as a singlet open shell system, and show a well defined edge effect.