

# Topological coordinates for nanotubes

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## Abstract

The topological coordinate method is a simple and effective approach for generating good initial coordinates for fullerene and nanotube carbon structures in molecular mechanics calculations. In this method some special eigenfunctions, the bi-lobal eigenfunctions of the Hückel Hamiltonian, or the adjacency matrix are used. It is based on a special connection between the electronic and geometric structure of fullerenes and nanotubes. We have found that the most efficient nanotube initial coordinates can be obtained with the four bi-lobal eigenvector method. The three bi-lobal eigenvector method gave relative good initial coordinates only if the two ends of the tube were closed. In both cases the scaling factors based on the Schrödinger equation of a particle in a rectangular box gave the best result.

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## 1. Introduction

The electronic structure of a polyhex single-walled carbon nanotube is governed by the diameter and chirality [1–5]. If the tube contains pentagonal and heptagonal faces too, its physical behavior depends on the topological properties as well [6–27], and the final geometrical structure can be determined only by some molecular mechanics calculation. For the relaxation process we need some good initial coordinates and various methods can be used in generating the input positions of the carbon atoms. One of them is the NiceGraph algorithm [20] and the other is the topological coordinate method [21,23]. In the NiceGraph algorithm a spring-embedder routine is used for optimizing the 3D drawing, and the topological coordinate method is based on the bi-lobal eigenvectors of the adjacency matrix of the graph.

Here we shall study the application of the topological coordinate method for nanotubes. In Ref. [25] we presented a version where the nanotube coordinates are obtained from those of the corresponding torus. Why do not we use algorithm developed for the fullerenes? What

are the influences of various scaling factors? These questions will be examined in this paper.

## 2. The topological coordinate method

Let  $\mathbf{A}$  be the adjacency matrix with elements  $A_{ij} = 1$ , if atoms  $i$  and  $j$  are adjacent and  $A_{ij} = 0$  otherwise. From this definition follows that  $\mathbf{H} = -\mathbf{A}$ , where  $\mathbf{H}$  is the Hückel Hamiltonian matrix with  $\alpha = 0$  and  $\beta = -1$ , where  $a$  is the diagonal matrix element and  $\beta$  is the non-zero non-diagonal matrix element of  $\mathbf{H}$ . It is assumed further that

$$a_1 > a_2 \geq a_3 \geq \dots \geq a_n, \quad (1)$$

if  $a_k$  is the  $k$ th eigenvalue of  $\mathbf{A}$  and  $\mathbf{e}^k$  is the corresponding eigenvector.

First we define the bi-lobal eigenvectors [21,22]. Vectors having this bi-lobal property can be identified by the graph-disconnection test: for a candidate vector, color all vertices bearing positive coefficients black, all bearing negative coefficients white, and all bearing a zero coefficient gray; now delete all gray vertices, all edges incident on gray vertices, and all edges connecting a black to a white vertex; if the graph now consists of exactly two connected components, one of black and one of white vertices, then the eigenvector is bi-lobal type [21,22,24].

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If  $\mathbf{c}^{k_1}$ ,  $\mathbf{c}^{k_2}$  and  $\mathbf{c}^{k_3}$  are the first three bi-lobal eigenvectors of  $\mathbf{A}$ , then the  $x_i$ ,  $y_i$  and  $z_i$  topological coordinates of the carbon atoms in a spherical carbon structure (fullerene) are:

$$x_i = S_1 c_i^{k_1}, \quad (2)$$

$$y_i = S_2 c_i^{k_2} \quad (3)$$

and

$$z_i = S_3 c_i^{k_3}, \quad (4)$$

where  $S_x = 1$  or  $S_x = 1/\sqrt{(a_1 - a_{k_x})}$  or any other appropriate scaling factor.

The topological coordinates of the torus are calculated from four bi-lobal eigenvectors  $\mathbf{c}^{k_1}$ ,  $\mathbf{c}^{k_2}$ ,  $\mathbf{c}^{k_3}$  and  $\mathbf{c}^{k_4}$ , as

$$x_i = S_1 C_i^{k_1} (1 + S_4 C_i^{k_4}), \quad (5)$$

$$y_i = S_2 C_i^{k_2} (1 + S_4 C_i^{k_4}), \quad (6)$$

$$z_i = S_3 C_i^{k_3}, \quad (7)$$

where  $S_1$ ,  $S_2$ ,  $S_3$  and  $S_4$  are scaling factors as before. In the construction of this formula we supposed that the position of an atom  $i$  on the toroidal surface is the sum of vectors  $\mathbf{R}_i$  and  $\mathbf{r}_i$ . The vector  $\mathbf{R}_i$  points from the center of gravity of the torus to a point on the circular spine, and vector  $\mathbf{r}_i$  points from there to the surface point  $i$  [24].

The topological coordinates of the nanotube are obtained from the corresponding torus by supposing periodicity at the ends of the nanotube [25]:

$$x_i = S_3 C_i^{k_3}, \quad (8)$$

$$y_i = S_4 C_i^{k_4}, \quad (9)$$

$$z_i = R \arccos(S_1 C_i^{k_1}/R) \quad \text{if } C_i^{k_2} \geq 0 \quad (10)$$

and

$$z_i = R(2\pi - \arccos(S_1 C_i^{k_1}/R)) \quad \text{if } C_i^{k_2} < 0. \quad (11)$$

Here the radius  $R$  is the average value of  $\mathbf{R}_i$  with the scaling of Ref. [25].

### 3. Applications for nanotubes

The two-dimensional periodic lattice structure can be generated by the translations,  $\mathbf{t} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2$ , where  $n_1$  and  $n_2$  are integers and  $\mathbf{a}_1$  and  $\mathbf{a}_2$  are unit vectors of the direct lattice. The unit vectors of the super cell are  $\mathbf{e}_1 = m_{11} \mathbf{a}_1 + m_{12} \mathbf{a}_2$  and  $\mathbf{e}_2 = m_{21} \mathbf{a}_1 + m_{22} \mathbf{a}_2$  with integers  $m_{11}$ ,  $m_{12}$ ,  $m_{21}$ ,  $m_{22}$ . For the construction of the topological coordinates of a two-dimensional periodic system we need the number of atoms in the unit cell (0,0) and the neighbors each of them. Using then the integers  $m_{11}$ ,  $m_{12}$ ,  $m_{21}$ ,  $m_{22}$  the matrix  $\mathbf{A}$  of the corresponding torus can be constructed by identifying the opposite edges of the super cell, and finally the topological coordinates are calculated by the Eqs. (8)–(11). Here we suppose that the

tube axis is parallel with the super cell unit vector  $\mathbf{e}_2$  and each nanotube can be characterized by the vector  $(m_{11}, m_{12}, m_{21}, m_{22})$ . Thus the topological coordinates can be obtained without knowing the unit vectors  $\mathbf{a}_1$ , and  $\mathbf{a}_2$  and without knowing the coordinates of the atoms in the unit cell.

In Figs. 1–6 we have presented the topological coordinates of the nanotube (3,2,-12,30) using various methods and  $S_x$  scaling factors. The best initial guess for nanotube geometry was obtained by Eqs. (8)–(11) and  $S_x = 1/\sqrt{(a_1 - a_{k_x})}$  with  $k_1 = 2$ ,  $k_2 = 3$ ,  $k_3 = 12$  and  $k_4 = 13$  in Fig. 1. In each cases of Figs. 1–6 the scaling factors  $S_x = 1/\sqrt{(a_1 - a_{k_x})}$  were better than those of  $S_x = 1$ .



Fig. 1. Topological coordinates obtained by Eqs. (8)–(11) with  $S_x = 1/\sqrt{(a_1 - a_{k_x})}$ ,  $k_1 = 2$ ,  $k_2 = 3$ ,  $k_3 = 12$  and  $k_4 = 13$  for the nanotube (3,2,-12,30). Both ends are open.

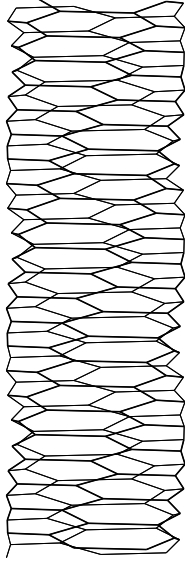


Fig. 2. Topological coordinates obtained by Eqs. (8)–(11) with  $S_z = 1$ ,  $k_1 = 2$ ,  $k_2 = 3$ ,  $k_3 = 12$  and  $k_4 = 13$  for the nanotube (3,2, -12,30). Both ends are open.

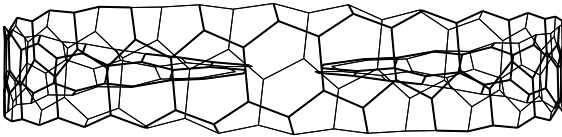


Fig. 3. Topological coordinates obtained by Eqs. (2)–(4) with  $S_z = \sqrt{a_1 - a_{k_z}}$ ,  $k_1 = 2$ ,  $k_2 = 11$  and  $k_3 = 12$  for the nanotube (3, 2, -12,30). Both ends are open.

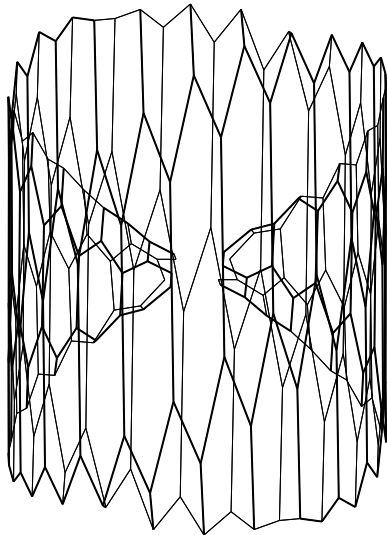


Fig. 4. Topological coordinates obtained by Eqs. (2)–(4) with  $S_z = 1$ ,  $k_1 = 2$ ,  $k_2 = 11$  and  $k_3 = 12$  for the nanotube (3, 2, -12, 30). Both ends are open.

These results can be explained by the fact that the scaling factors  $S_z = 1/\sqrt{a_1 - a_{k_z}}$  are based on the solutions of the Schrödinger equation for a particle in a rectangular box [21]. That is



Fig. 5. Topological coordinates obtained by Eqs. (2)–(4) with  $S_z = 1/\sqrt{a_1 - a_{k_z}}$ ,  $k_1 = 2$ ,  $k_2 = 12$  and  $k_3 = 13$  for the nanotube (3, 2, -12, 30). Both ends are closed.

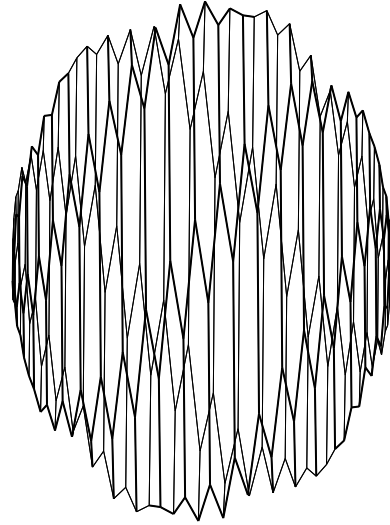


Fig. 6. Topological coordinates obtained by Eqs. (2)–(4) with  $S_z = 1$ ,  $k_1 = 2$ ,  $k_2 = 12$  and  $k_3 = 13$  for the nanotube (3, 2, -12,30). Both ends are closed.

$$\psi_{n_x, n_y, n_z} = \sin\left(\frac{n_x \pi}{L_x} x\right) \sin\left(\frac{n_y \pi}{L_y} y\right) \sin\left(\frac{n_z \pi}{L_z} z\right) \quad (12)$$

and

$$E_{n_x, n_y, n_z} = \frac{\hbar^2 \pi^2}{2m} \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right), \quad (13)$$

are the solutions, where  $L_x, L_y, L_z$  are the sides of the box and  $n_x, n_y, n_z$  are integers. Thus:

$$a_1 = E_{1,1,1} = \frac{\hbar^2 \pi^2}{2m} \left( \frac{1^2}{L_x^2} + \frac{1^2}{L_y^2} + \frac{1^2}{L_z^2} \right), \quad (14)$$

$$a_x = E_{2,1,1} = \frac{\hbar^2 \pi^2}{2m} \left( \frac{2^2}{L_x^2} + \frac{1^2}{L_y^2} + \frac{1^2}{L_z^2} \right), \quad (15)$$

$$a_y = E_{1,2,1} = \frac{\hbar^2 \pi^2}{2m} \left( \frac{1^2}{L_x^2} + \frac{2^2}{L_y^2} + \frac{1^2}{L_z^2} \right) \quad (16)$$

and

$$a_z = E_{1,1,2} = \frac{\hbar^2 \pi^2}{2m} \left( \frac{1^2}{L_x^2} + \frac{1^2}{L_y^2} + \frac{2^2}{L_z^2} \right), \quad (17)$$

give the scaling  $S_z = 1/\sqrt{a_1 - a_{k_z}}$ .

Figs. 3 and 4 show that the topological coordinates obtained by Eqs. (2)–(4) can not be used directly for a tube, as the eigenvectors  $k_1 = 2$ ,  $k_2 = 11$ ,  $k_3 = 12$  “remember” to the eigenvectors  $k_1 = 2$ ,  $k_3 = 12$ ,  $k_4 = 13$  of the corresponding torus. This is why the two ends of the tube turn back using Eqs. (2)–(4). At the ends of the tube there are ten two-connected atoms and in the Theorem of Lovász and Schrijver [28] the condition that the graph be three-connected is essential for a proper embedding on a sphere. For the connection between the topological coordinate methods and the null space embedding of graphs see for example [25]. We did not obtain the turning back after eliminating the two-connected atoms with addition of two pentagons at the two ends of the tube. See Figs. 5 and 6.

#### 4. Conclusions

With the help of the bi-lobal eigenvectors of the  $\mathbf{A}$  adjacency matrix good initial Descartes coordinates can be generated for fullerenes and nanotubes. In appropriate energy units the  $\mathbf{A}$  is the negative Hückel Hamiltonian ( $\mathbf{A} = -\mathbf{H}$ ) and one can say, that in this method some electronic eigenfunctions are used in the construction of the atomic positions. Here we examined the three and four bi-lobal methods, and it was found that the best coordinates were obtained using four bi-lobal eigenvectors and scaling coefficients based on the solutions of the Schrödinger equation for a particle in a rectangular box. The three bi-lobal eigenvector method gave relative good initial coordinates only if the two ends of the nanotube were closed.

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#### References

- [1] Mintmire JW, Dunlap BI, White CT. Are fullerene tubules metallic? *Phys Rev Lett* 1992;68:631–4.
- [2] Hamada N, Sawada S, Oshiyama A. New one-dimensional conductors: graphitic microtubules. *Phys Rev Lett* 1992;68:1579–81.
- [3] Saito R, Fujita S, Mitsutaka F, Dresselhaus G, Dresselhaus MS. Electronic structure of graphene tubules based on  $C_{60}$ . *Phys Rev B* 1992;46:1804–11.
- [4] Dresselhaus MS, Dresselhaus G, Eklund PC. In: *Science of fullerenes and carbon nanotubes*. San Diego, Boston, New York, London, Sydney, Tokyo, Toronto: Academic Press; 1996. Chapter 19.
- [5] Ceulemans A, Chibotaru LF, Bovin SA, Fowler PW. The electronic structure of polyhex carbon tori. *J Chem Phys* 2000;112:4271–8.
- [6] Mackay AL, Terrones H. Diamond from graphite. *Nature* 1991;352:762.
- [7] Ihara S, Itoh S, Kitakami J-i. Toroidal forms of graphitic carbon. *Phys Rev B* 1993;47:12908–11.
- [8] Ihara S, Itoh S, Kitakami J-i. Helically coiled cage forms of graphitic carbon. *Phys Rev B* 1993;48:5643–7.
- [9] Itoh S, Ihara S. Toroidal forms of graphitic carbon. II. elongated tori. *Phys Rev B* 1993;48:8323–8.
- [10] Amelinckx S, Zhang XB, Bernaerts D, Zhang XF, Ivanov V, Nagy JB. A formation mechanism for catalytically grown helix-shaped graphite nanotubes. *Science* 1994;265:635–9.
- [11] Akagi K, Tamura R, Tsukada M, Itoh S, Ihara S. Electronic structure of helically coiled cage of graphitic carbon. *Phys Rev Letters* 1995;74:2307–10.
- [12] Avron JE, Berger J. Tiling rules for toroidal molecules. *Phys Rev B* 1995;51:1146–9.
- [13] Akagi K, Tamura R, Tsukada M, Itoh S, Ihara S. Electronic structure of helically coiled carbon nanotubes: relation between the phason lines and energy band features. *Phys Rev B* 1996;53:2114–20.
- [14] Volodin A, Ahlskog E, Seynaeve E, van Haesendonck C. Imaging the elastic properties of coiled carbon nanotubes with atomic force microscopy. *Phys Rev Letters* 2000;84:3342–5.
- [15] Bíró LP, Lazarescu SD, Thiry PA, Fonseca A, Nagy JB, Lucas AA, et al. Scanning tunneling microscopy observation of tightly wound, single-wall coiled carbon nanotubes. *Europhys Lett* 2000;50:494–500.
- [16] Terrones H, Terrones M, Hernández E, Grobert N, Charlier J-C, Ajayan PM. New metallic allotropes of planar and tubular carbon. *Phys Rev Lett* 2000;84:1716–9.
- [17] László I, Rassat A. Toroidal and spherical fullerene-like molecules with only pentagonal and heptagonal faces. *Int J Quantum Chem* 2001;84:136–9.
- [18] Diudea MV, Kirby EC. The energetic stability of tori and single-wall tubes. *Fullerene Sci Technol* 2001;9:445–65.
- [19] Diudea MV, Pârv B, Kirby EC. Azulenics tori. *MATCH-Commun Math Comput Chem* 2003;47:53–70.
- [20] Pisanski T. Vega quick reference manual and vega graph gallery. Ljubljana, 1995 (Also at <http://vega.ijp.si>).
- [21] Manolopoulos DE, Fowler PW. Molecular graphs, point groups, and fullerenes. *J Chem Phys* 1992;96:7603–14.
- [22] Fowler PW, Manolopoulos DE. In: *An Atlas of Fullerenes*. Clarendon Press; 1995. p. 101–4. Chapter 5.
- [23] Graovac A, Plavšić D, Kaufman M, Pisanski T, Kirby EC. Application of the adjacency matrix eigenvectors method to geometry determination of toroidal carbon molecules. *J Chem Phys* 2000;113:1925–31.
- [24] László I, Rassat A, Fowler PW, Graovac A. Topological coordinates for toroidal structures. *Chem Phys Lett* 2001;342:369–74.
- [25] László I, Rassat A. The geometric structure of deformed nanotubes and the topological coordinates. *J Chem Inf Comput Sci* 2003;43:519–24.
- [26] Kirby EC. On toroidal azulenooids and other shapes of fullerene cage. *Fullerene Sci Technol* 1994;2:395–404.
- [27] Deza M, Fowler PW, Shtogrin M, Vietze K. Pentaheptite modifications of the graphite sheet. *J Chem Inf Comput Sci* 2000;40:1325–32.
- [28] Lovász L, Schrijver A. On the null space of a colin de verdière matrix. *Ann I Fourier (Grenoble)* 1999;49:1017–26.