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Topological coordinates for toroidal structures

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Abstract

Physically realistic 3D geometries for toroidal trivalent networks can be produced from graph theoretical information alone, using the eigenvectors resulting from diagonalisation of the vertex adjacency matrix. Arguments from the problem of a quantum particle constrained to move on a surface show that three vectors suffice for zero-genus spherical cages, whereas four are needed for decorations of surfaces with genus 1 (in contrast to previous suggestions). Solutions for the problems arising from the systematic high degeneracies in the spectra of polyhex tori are proposed.

1. Introduction

For many purposes it is useful to be able to assign a set of physical cartesian coordinates to a structure that is defined only by its graph, i.e. by the adjacencies of its vertices. Coordinate realisations allow, for example, drawing, optimisation, energy calculation and symmetry assignment for chemical structures. A simple solution to the problem for spherical polyhedra (whose graphs are three-connected and planar) was proposed in earlier work [1,2]. It relies on the correspondence between eigenvectors of the adjacency matrices of such graphs and spherical harmonic functions. Here we consider the extension of the method from S^2, the sphere, to T^2, the torus. Toroidal molecules are of topical interest in carbon chemistry and physics [3–10] and may be expected to exhibit novel magnetic properties [9,11,12]. Some difficulties in obtaining good drawings of toroidal polyhexes and related molecules have been noted in the literature [14], but these can be solved by the extension made in the present Letter of the harmonic approach to 'topological coordinates'.

2. Background

We follow [1,2]. Let **A** be the adjacency matrix of the n-vertex graph, with elements $A_{ij} = 1$ if atom (vertex) i is bonded (joined by an edge) to atom (vertex) j, and $A_{ij} = 0$ otherwise. Let $\mathbf{C}^k$ be the kth eigenvector of **A**, and a_k the corresponding eigenvalue, with all $\mathbf{C}^k$ chosen to form an orthogonal set. Then,

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$$\sum_j^n A_{ij} C_j^k = a_k C_i^k, \tag{1}$$

$$\sum_j^n C_j^k C_j^l = \delta_{kl}. \tag{2}$$

Assume that the eigenvalues are labelled in descending order,

$$a_1 > a_2 \geqslant a_3 \geqslant \cdots \geqslant a_n. \tag{3}$$

$\mathbf{C}^1$ is then the totally symmetric, non-degenerate vector, which has every coefficient C_j^1 of the same sign (and equal to $1/\sqrt{n}$, if the graph is regular, as for the trivalent fullerenes).

When the graph can be embedded in S^2, $\mathbf{C}^1$ corresponds to the spherically symmetric S harmonic (angular momentum $L = 0$). The basis of the 'topological coordinate' method is then to identify three further vectors $\mathbf{C}^{k_x}$, $\mathbf{C}^{k_y}$, $\mathbf{C}^{k_z}$ that correspond to the next spherical harmonic set i.e., to three real components P_α $(\alpha = x, y, z)$ with angular momentum $L = 1$. As the value of P_α at a point $\mathbf{r_j} = (x_j, y_j, z_j)$ on the sphere is, apart from normalisation, just equal to α_j, the entries in these vectors can be read directly as coordinates or can be scaled to give a polyhedron of suitable overall size or average edge length.

The essential feature of a harmonic P_α is that it consists of two lobes of opposite sign, separated by a single nodal plane. Vectors having this bi-lobal property can be identified by the graph-disconnection test: for a candidate vector, colour all vertices bearing positive coefficients black, all bearing negative coefficients white, and all bearing a zero coefficient grey; now delete all grey vertices, all edges incident on grey 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 of P type. This is a more formal statement of the procedure already used in [1,2] and is applicable provided the original graph covers the sphere sufficiently densely i.e., provided that n is sufficently large, so that at least for the lower harmonics, there will be at most one nodal surface passing through any given edge (see Fig. 15 of [14] for what can happen in a counter example).

3. Application to tori

On the torus there are not three but four mutually orthogonal bi-lobal harmonic functions (P_x, P_y, P_z and P_r) which span representations Π_u, Σ_u^+ and Σ_g^+, respectively, of the parent point group ($D_{\infty h}$) appropriate to an undecorated torus with rotational symmetry about z. The four nodal patterns are shown in Fig. 1. Notice that although their symmetries in $D_{\infty h}$ are different, P_z and P_r can be interchanged by an 'anapolar' [13] motion where all points move on circles about the internal circular spine of the torus; the harmonics P_x and P_y are of course exchanged by a rotation about the z axis.

Given the four eigenvectors $\mathbf{C}^{k_x}$, $\mathbf{C}^{k_y}$, $\mathbf{C}^{k_z}$, $\mathbf{C}^{k_r}$ corresponding to these functions, the cartesian coordinates of vertex i can be defined by a vector construction in which each point on T^2 is assigned a 'latitude' by its position on a local circular cross-section normal to the xy plane, and a 'longitude' by the angular position of its projection onto the xy plane. (The two sets of curves on a ruled solid torus are sometimes known as 'meridians' and 'longitudes', where the distinction is that a meridian bounds a disc inside the solid, but a longitude bounds a disc in the exterior space [15].) The position of the point is the sum of a vector $\mathbf{R}$ from the centre of gravity of the torus to a point on the circular spine, and a vector $\mathbf{r}$ from there to the surface (see Fig. 2). The size and aspect ratio of the torus are governed by the two radii $R = |\mathbf{R}|$ and $r = |\mathbf{r}|$ (see Fig. 2).

The topological ansatz for the coordinates of vertex i is therefore

$$X_i = S_x C_i^{k_x}(1 + S_r C_i^{k_r}), \quad Y_i = S_y C_i^{k_y}(1 + S_r C_i^{k_r}),$$
$$Z_i = S_z C_i^{k_z}, \tag{4}$$

where S_x, S_y, S_z, S_r are the scaling factors which reflect the radii $\mathbf{R}$ and $\mathbf{r}$ and may be chosen according to a recipe such as [1,2]

$$S_\alpha = 1 \Big/ \sqrt{(a_1 - a_{k_\alpha})}. \tag{5}$$

Notice that the above Eq. (4) uses four eigenvectors and not three as a direct analogy with the spherical case would suggest. The four are necessary to represent the full set of degrees of freedom

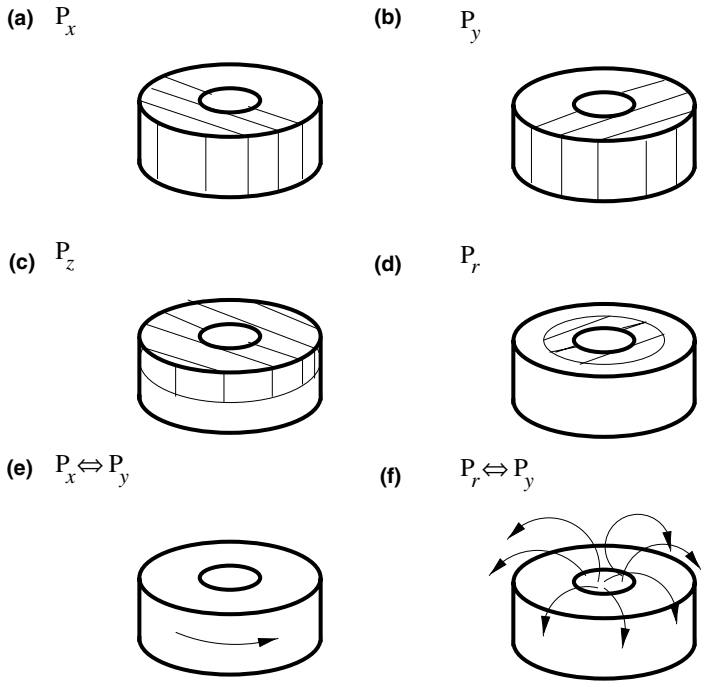

Fig. 1. The four orthogonal, bi-lobal, surface harmonic functions on the torus and their interconversion motions.

of the torus. It can be seen from (4) that if, for example, the $\mathbf{C}^{k_r}$ vector is neglected, (or S_r set to zero) the torus will be reduced to a flat cylindrical strip. The inequivalent roles of the four vectors in (4) arise from our choice of *xy* as the equatorial plane. From a topological point of view, the surface of the torus can be constructed by identifying opposite edges of a rectangle, and the order in which this is done determines which pair of coordinates is *xy* and which is *Rr* in the subsequent three-dimensional embedding. Reversing this order, or making other transformations of coordinates allowed under the invariance of the torus, can produce physically distinct realisations with the same nominal connectivity [4]; our choice is appropriate to chemical graphs, which tend for steric reasons to be realised as 'long, thin' rather than 'short, fat' tori, and it generally gives physically realistic coordinates in which geometric proximity and graph-theoretical adjacency are in agreement.

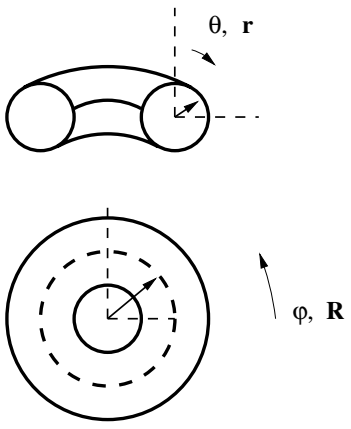

Fig. 2. Definition of angular and radial coordinates for the torus.

It appears that at least four vectors can always be found by explicit application of the disconnection test to the full set of eigenvectors. However the surface-harmonic picture gives a strong hint as to which vectors these will be, especially when there is high symmetry. In a sufficiently large graph and in the absence of extra accidental degeneracy the usual particle-on-a-surface arguments

suggest $(k_x, k_y) = (2, 3)$, which form a degenerate pair of eigenvectors for tori of $D_{nh}, D_{nd}, C_{nh}, C_{nv}$ $(n \geqslant 3)$ symmetry.

4. Results

4.1. Tori with pentagonal and heptagonal faces

From Euler's theorem it is mathematically possible to cover the torus entirely with hexagonal faces to form trivalent carbon frameworks, and these hypothetical polyhex tori have been intensively studied from the point of view of π-electron theory [4,9]. It is useful, however, to introduce non-hexagonal faces to relieve the considerable steric strain of the pure polyhex [3].

Fig. 3 shows an example of a 5, 6, 7 framework in which the present method has been used to construct topological coordinates. The resulting geometry is a plausible starting point for further chemical investigations.

In contrast, the structures produced with only three eigenvectors are seen to be unphysical, in one case considerably flattened into a cylinder, in the other less distorted but still so nearly cylindrical that geometrically close neighbours no longer correspond to adjacent vertices of the graph. In the three-vector method a choice must be made between P_z and P_r vectors; in the full four-vector method, both are given appropriate weight, leading to a properly rounded toroidal structure. Similar results can be obtained for many other examples of this class of graphs.

4.2. The polyhex torus

Purely hexagonal toroidal frameworks present some new features for the method. Polyhex tori can be considered as constructed from a parallelogram-shaped patch of hexagons defined by two lattice vectors $\mathbf{a_1} = a(\sqrt{3}, 1)/2$ and $\mathbf{a_2} = a(\sqrt{3}, -1)/2$, where opposite edges of the parallelogram have been identified [9]. This construction uses four integers (n, m, p, q) for the chiral vector $\mathbf{C}_h = n\mathbf{a_1} + m\mathbf{a_2}$ and the twisting vector $\mathbf{T} = p\mathbf{a_1} + q\mathbf{a_2}$. (A further reduction is possible by appropriate choice of the unit parallelogram [4].) Fig. 4 shows four typical

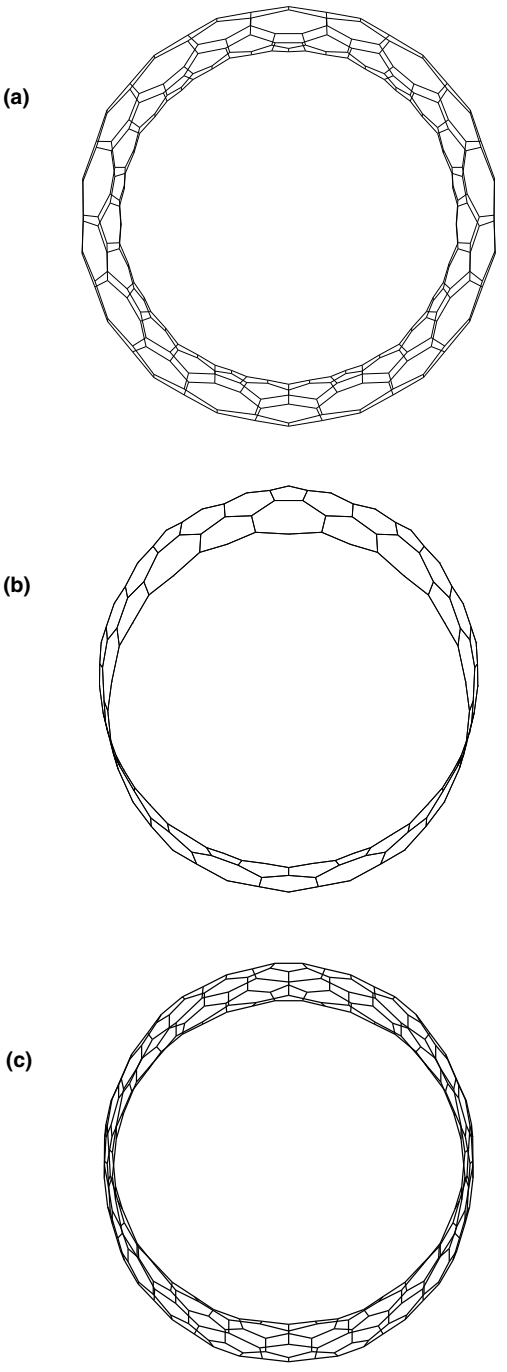

Fig. 3. A toroidal framework C_{270} composed of pentagonal, hexagonal and heptagonal rings. Drawn from coordinates based on: (a) four eigenvectors $(2, 3, 10, 13)$ using Eq. (4) of the present work; (b) three eigenvectors $(2, 3, 10)$ [14]; (c) three eigenvectors $(2, 3, 13)$ [14].

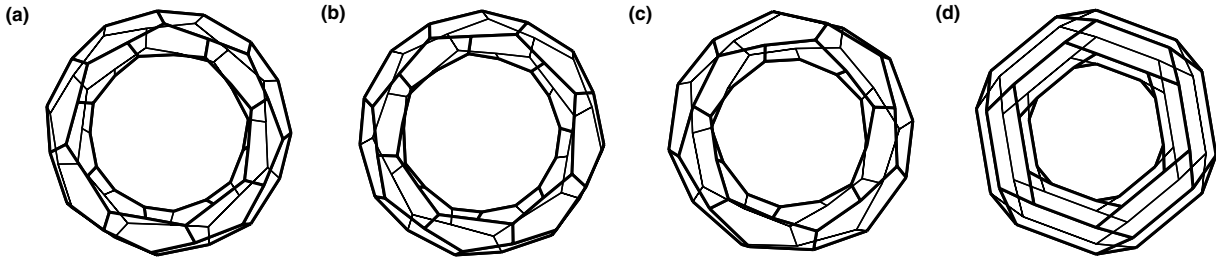

Fig. 4. Polyhex toroidal frameworks drawn from their topological coordinates [Eq. (4)]: (a) $(n,m,p,q) = (3,2,7,-8)(k_x,k_y,k_z,k_r) = (2,3,4,5)$; (b) $(n,m,p,q) = (3,2,4,-10)(k_x,k_y,k_z,k_r) = (2,3,4,5)$; (c) $(n,m,p,q) = (3,2,5,-7)(k_x,k_y,k_z,k_r) = (2,3,4,5)$; (d) $(n,m,p,q) = (5,0,3,-6)(k_x,k_y,k_z,k_r) = (2,3,4,5)$.

polyhex tori, drawn from the topological coordinate expressions (4).

The toroidal polyhex has systematic degeneracies. According to [9] the eigenvalues $a_K > 0$ are the following:

$$a_K = (1 + 4\cos(K_y)\cos(K_x) + 4\cos^2(K_y))^{\frac{1}{2}}, \qquad (6)$$

with

$$K_x = K_x(l_t, l_n) = \pi\frac{(l_t(m-n) + l_n(p-q))}{(mp - nq)} \qquad (7)$$

and

$$K_y = K_y(l_t, l_n) = \pi\frac{(l_t(m+n) - l_n(p+q))}{(mp - nq)}. \qquad (8)$$

With a simple trigonometric transformation we obtain:

$$\begin{aligned} a_K &= a(l_t, l_n) \\ &= (3 + 2(\cos(K_y - K_x) \\ &\quad + \cos(K_y + K_x) + \cos(2K_y)))^{\frac{1}{2}}. \end{aligned} \qquad (9)$$

From this equation it follows that $a(0,0) = 3$ and $a(l_t, l_n) = a(-l_t, -l_n)$, and thus each energy level except $a = +3$ and $a = -3$ is at least twofold degenerate [4].

The necessary condition for a straightforward use of the method of topological coordinates is that there should be at least four two-lobe eigenvectors and that the corresponding energy levels should be at most twofold degenerate. In practice we have always found at least four eigenvectors with two lobes, but there are some cases when they form part of larger degenerate sets. Degeneracies in polyhex torus graphs are often higher than 2. For example, if the polyhex torus is a leapfrog, i.e., with both $n - m$ and $p - q$ divisible by 3, then the eigenvalue formula yields degeneracy 6 for all but special eigenvalues. Sixfold degeneracies also occur, for example, for $(n,m,p,q) = (3,2,2,-5)$. A solution to the problem is to use an expanded torus as follows. If a degeneracy problem is encountered for the parameters (n,m,p,q), there is always an integer s, such that the method can be used for the parameters (n,m,sp,sq) corresponding to s-fold repetition of the unit that in (n,m,p,q) would comprise the whole torus. One of these units can then be transformed from an arc of $2\pi/s$ radian to a full circle to span the torus with the original parameters.

4.3. The square lattice

The main chemical applications of the method are likely to be to trivalent frameworks, but it can be used for others. In the case of square lattices which form four regular graphs on the torus we can carry out the construction and calculation of eigenvalues in the same way as for the polyhex. Four independent integer parameters (n,m,p,q) can be applied for the square-covered torus, but now with $\mathbf{a_1} = a(0,1)$, and $\mathbf{a_2} = a(1,0)$.

The discussion of degeneracies follows along the same lines as before, but now:

$$a_K = a(l_t, l_n) = 2(\cos(K_x) + \cos(K_y)) \qquad (10)$$

with

$$K_x = K_x(l_t, l_n) = \pi\frac{(-l_t n + l_n p)}{(mp - nq)} \qquad (11)$$

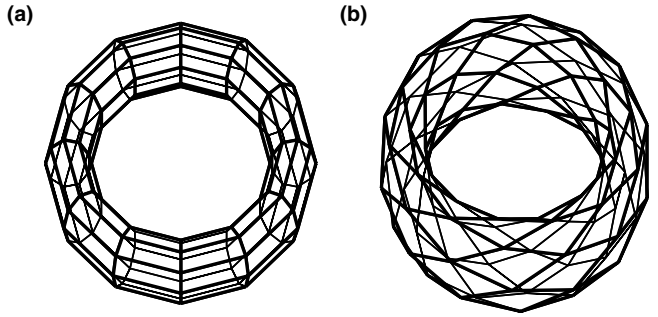

Fig. 5. Square-lattice toroidal polyhedra, drawn from their topological coordinates [Eq. 4)]: (a) $(n,m,p,q) = (12,0,0,9)(k_x,k_y,k_z,k_r) = (2,3,4,5)$; (b) $(n,m,p,q) = (12,3,5,9)(k_x,k_y,k_z,k_r) = (2,3,4,5)$.

and

$$K_y = K_y(l_t, l_n) = \pi \frac{(l_t m - l_n q)}{(mp - nq)}. \tag{12}$$

Fig. 5 shows two typical cases.

5. Conclusion

The knowledge that a given trivalent graph is to be realised on the surface of a torus rather than a sphere can be used to give physically realistic 3D geometries based on four rather than three eigenvectors of the vertex adjacency matrix. The method is straightforward and gives good starting coordinates of potential use in many applications. Toroidal graphs seem to present more problems of systematic degeneracy than their spherical counterparts, but at least for those graphs that are of interest as possible toroidal carbon networks, these problems can be sidestepped. Similar extensions of the three-vector spherical topological coordinate method are readily devised for frameworks embedded in orientable surfaces of higher genus, where for a surface of genus g, $3 + g$ vectors would give a complete specification of coordinates.

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