Symmetry of arbitrary layer rolled-up nanotubes

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Rolling up of a layer with arbitrary lattice gives nanotube with very reach symmetry, described by a line group which is found for arbitrary diperiodic group of the layer and chiral vector. Helical axis and pure rotations are always present, while the mirror and glide planes appear only for specific chiral vectors in rhombic and rectangular lattices. Nanotubes are not translationally periodical unless layer cell satisfies very specific conditions. Physical consequences, including incommensurability of carbon nanotubes, are discussed.

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INTRODUCTION

Large line group symmetry of carbon nanotubes (NTs) is substantial [1, 2] in predicting their unique properties [3, 4]. The underlying 2D hexagonal lattices enabled to apply essentially the same symmetry to several inorganic NTs [5]. However, besides recent result on the rectangular lattices [6], the symmetry of NTs related to the other kinds of 2D lattices has never been considered, despite rapidly increasing number of the reported types: BC2N [7], ternary borides [8], carbon pentaheptides and Haekkelites [9], ZnO nanorings [10], etc.

Here we fill in this gap presenting quite general result: full symmetry of the rolled-up arbitrary layer is found. NT may be without translational periodicity, but its symmetry is always described by a line group. As discussed, this has many far reaching physical consequences, including reconsideration of carbon NTs’ symmetry.

LINE GROUPS

In contrast to 2D and 3D crystals, quasi-1D ones are not subdued to the crystallographic restrictions on the rotational axis, while in some cases helical ordering substitutes translational periodicity. Consequently, number of different symmetry groups, line groups, of quasi-1D systems is infinite, in contrast to 80 diperiodic and 273 space groups. Only 75 line groups are subgroups of the latter; they are known as rod groups [11].

Line groups are classified within thirteen families (Tab. I). Each group is a product \( L = ZP_n \) of an axial point group \( P_n \) and an infinite cyclic group \( Z \). Thus \( P_n \) is one of \( C_n, S_{2n}, C_{nh}, D_{nv}, C_{nv}, D_{nd}, D_{nh} \), where \( n = 1, 2, \ldots \) is the order of its principle axis (\( z \)-axis, by convention). Group of the generalized translations \( Z \) is either screw axis \( TQ(f) \) or a glide plane \( T'(f) \), generated by \( (CQ)[f] \) (Koster-Seitz symbol), i.e. rotation for \( 2\pi/Q \) around the \( z \)-axis followed by translation for \( f \) along the same axis (\( Q \geq 1 \) is a real number), and \( (σ_v) \), respectively. While pure translation (for \( 2f \)) pertains to \( T'(f) \), group \( TQ(f) = T^*_Q(f) \) contains pure translation (for \( fq \)) only for rational \( Q = q/r \) (\( r \) and \( q \) integers).

FIG. 1: Top: Chiral vectors \( e \), with corresponding \( a \) (in the commensurate cases), \( z \) (all \( z \) are on the dashed line) and \( f \). Left: \( A_1 = (12, \sqrt{2}) \) and \( A_2 = (\frac{1}{\sqrt{2}}, 6) \) \((X = w = 4, Y = J + X = 2\sqrt{2}/73, x = 0, y = 1) \), with \( c = (3, 6) \), \( z = (0, 1) \) and \( L^{(1)} = T^1_{12}(3\sqrt{2} - \frac{1}{2})C_3 \) Middle: rhombic layer with \( α = 70° \), \( c = (3, 3) \), \( z = (0, 1) \) and \( L^{(1)} = T_{0}(a/2 ≈ 0.57A_1)C_3 \). Right: rectangular layer with \( A_1/A_2 = π/3 \), \( c = (3, 0) \), \( z = (1, 1) \), \( L^{(1)} = T^{1}_{1}(a = A_2)C_3 \) and \( c' = (3, 3) \), \( z' = (0, 1) \), \( L^{(1)'} = T^{1}_{3}(\frac{2}{\sqrt{9+π^2}}A_1)C_3 \). Bottom: corresponding nanotubes.

All the combinations \( (CQ)[f]^\dagger C_n^a \) of rotations around the principle axis and translations form roto-helical subgroup \( L^{(1)} \) (first family line group) of \( L \). In the course of rolling it emerges from the 2D lattice translations. For the first family line groups \( L^{(1)} = L \); for the groups from the 2-8 families \( L^{(1)} \) is a halving subgroup, while for the families 9-13 \( L^{(1)} \) is a quarter subgroup. Consequently, when \( L^{(1)} \) is known, to build up the whole line group it remains to find if there are additional generators (mirror/glide plane and/or \( U \)-axis) allowed both by the symmetry of the elementary cell of the specific layer and chiral vector.

Note that \( Q \) is not unique, and therefore the conven-
ntion [6] is introduced: Q is the greatest finite among $Q_i = Qn/(Qs + n)$; for the commensurate groups this $Q$ is written as $Q = q/r$ with $q$ being multiple of $n$, $q = qn$, and $r$ is coprime to $q$, while the translational period is $a = qf$. For example, the group combining pure translations $T(f = a)$ with $C_n$ is $T(aC_n) = T'_n(a)C_n$.

Only the line groups from the first and fifth family may have irrational $Q$, in which case they refer to the incommensurate systems, i.e. helically ordered but with no translational periodicity. The other families are characterized by $Q$ equal to $n$ or $2n$, i.e. these groups are achiral $T(f = a)$ (symmorphic line groups), $T_{2n}(f = a/2)P_n$ or $T'(f = a/2)P_n$.

**ROTO-HELMICAL TRANSFORMATIONS**

We consider 2D lattice, with a basis $A_1$ and $A_2$ ($A_1 \geq A_2$) at the angle $\alpha \in (0, \pi/2]$ and define dimensionless parameters $X$ and $Y$:

$$X = \frac{A_1^2}{A_2} \geq 1, \quad Y = \frac{A_1}{A_2} \cos \alpha \geq 0. \quad (1)$$

NT $(n_1, n_2)$ is obtained by folding the layer in a way that the chiral vector $c = (n_1, n_2) = n_1A_1 + n_2A_2$ becomes circumference of the tube (Fig. 1). Alternatively, NT is defined by length $c$ (giving the tube’s diameter $D = c/\pi$) and slope $\theta$ (called chiral angle) of $c$:

$$c = A_2\sqrt{n_1^2 X + n_2^2 + 2n_1n_2 Y}, \quad \sin \theta = n_2A_2/c. \quad (2)$$

It is enough to consider NTs with $n_2 \geq 0$, i.e. $0 \leq \theta < \pi$, as the nanotube $(-n_1, -n_2)$ is same with $(n_1, n_2)$.

The translations of the layer become roto-helical operations on the tube, i.e. two-dimensional translational group is folded into $L^{(1)} = T(f)C_n$. Simple geometry and some number theory suffice to find the parameters $Q$, $n$ and $f$ [12]:

$$n = \gcd(n_1, n_2), \quad (3a)$$

$$f = \frac{\sin \alpha}{\sqrt{n_1^2 X + n_2^2 + 2n_1n_2 Y}}. \quad (3b)$$

$$Q = \frac{n}{n_1 z_1 X + n_2 z_2 + (n_1 z_2 + n_2 z_1) Y}. \quad (3c)$$

Here, $z = (z_1, z_2)$ is the closest to the line perpendicular to $c$ (but not on this line, Fig. 1) lattice vector from the series

$$(z_1 s, z_2 s) = z_0 + s(n_1, n_2), \quad s = 0, \pm 1, \ldots \quad (4)$$

$$z_0 = \begin{cases} (0, 1), & \text{if } c = (0, n), \\ (-1, 0), & \text{if } c = (0, n), \\ \left(\frac{n_2}{n_1}, \frac{n_2(n_1 - 1)}{n_1}, \frac{n_2(n_1 - 1)}{n_1}\right), & \text{otherwise.} \end{cases} \quad (5)$$

The Euler function $\varphi(x)$ gives the number of co-primes with $x$ which are less than $x$.

In conclusion, the roto-helical part $L^{(1)}$ of the NT symmetry generates the whole tube from a single 2D unit cell. The symmetry parameters $f$ and $Q = Q/n$ depend only on the reduced chiral vector $\tilde{c} = c/n = n_1A_1 + n_2A_2$, and thus they are the same for the ray of the NTs $n(n_1, n_2)$ differing by the order $n$ of the principle axis.

**Commensurability**

Instead of analyzing when (3c) gives rational $Q$, commensurability condition of NT is found by a direct check of existence of NT’s translational period $a$. Obviously, if exists, $a$ is the length of the minimal lattice vector $a = a_1A_1 + a_2A_2$ orthogonal onto the chiral vector. So we look for solvability (in coprime integers $a_i$) of

$$\tilde{c} \cdot a = a_2\tilde{n}_2 + a_1\tilde{n}_1X + (a_2\tilde{n}_1 + a_1\tilde{n}_2)Y = 0. \quad (6)$$

When solvable, the period of the tube is

$$a = A_2\sqrt{a_1^2 X + a_2^2 + 2a_1a_2 Y}. \quad (7)$$

Further, as $q$ is the number of 2D lattice unit cells within a translational period of a NT, the surface areas equality, $qA_1A_2 \sin \alpha = ca$, gives:

$$q = n\frac{\tilde{c}a}{A_2^2 \sqrt{X - Y^2}}. \quad (8)$$

Finally, $r$ is to be found from (3c).

To discuss solvability of (6), we note that only $X$ and $Y$ may be irrational. As the reals are an infinite dimensional vector space over the rational numbers, for solvability in rational $a_i$ (then also integral solutions exist) it is necessary that 1, $X$ and $Y$ are rationally dependent: either both $X$ and $Y$ are rational, or there are rational $w$, $x$ and $y$ (with $x \neq y$ as $X > Y$) and irrational $J$, such that $X = w + xJ$ and $Y = w + yJ$.

For both $X$ and $Y$ rational, Eq. (6) becomes a (rational) proportion between $a_1$ and $a_2$. All the NTs $(n_1, n_2)$ are commensurate with [12]:

$$q = n\frac{2n_1\tilde{n}_2XY + \tilde{n}_1X Y + \tilde{n}_2XY}{\gcd(\tilde{n}_1XY + \tilde{n}_2XY - \tilde{n}_1X Y + \tilde{n}_1XY)}, \quad (9)$$

$$a = (\tilde{n}_1XY + \tilde{n}_2XY - \tilde{n}_1X Y - \tilde{n}_1XY) \quad \gcd(\tilde{n}_1XY + \tilde{n}_2XY - \tilde{n}_1X Y + \tilde{n}_1XY)) \quad (10)$$

In the other case, rational and irrational parts of (6) are system of two homogeneous equations in $a_i$, solvable when its determinant vanishes:

$$\tilde{n}_1^2w(y - x) - \tilde{n}_1\tilde{n}_2x - \tilde{n}_2^2y = 0. \quad (11)$$

This constraint on $\tilde{n}_1$ and $\tilde{n}_2$ singles out a subset of the chiral vectors yielding commensurate NTs. Note that solutions may not exist (rationals are not algebraically closed). When exist, all the chiral vectors $n\tilde{c}$
Besides, interchanging roles of \( \tilde{c} \) and \( \alpha \), we get NTs with period \( \tilde{c} \), orthogonal onto chiral vectors \( n\alpha \). Hence, in such a lattice commensurate NTs lie on two perpendicular lines.

For \( \tilde{n}_2 \neq 0 \), the constraint (11) becomes

\[
\tilde{n}_1 = x + \frac{\sqrt{x^2 - 4wxy + 4w^2}}{2w(y-x)} = \nu_{\pm},
\]

and \( \tilde{n}_1/\tilde{n}_2 \) is rational only if \( \sqrt{x^2 - 4wxy + 4w^2} \) is. The commensurate NTs are \( \tilde{c}^{\pm} = \alpha^{\pm} = (\tilde{\tau}_a, \tilde{\tau}_b) \), giving \( q = n(\nu_{\pm}, \tilde{\tau}_a - \tilde{\tau}_b) \) and \( a^{\pm} = A_2\sqrt{L_{\pm}^2 + \tilde{\tau}_b^2}X + 2\nu_{\pm}\tilde{\tau}_bY \).

The case \( \tilde{n}_2 = 0 \) appears if and only if \( w = 0 \) and \( y = X \) (i.e., \( j = X \) and \( x = 1 \)). Then the ray orthogonal onto \( \tilde{c}^+ = (1,0) \) is obtained as \( \tilde{c}^- = (\tilde{\tau}, y) \). The periods are \( a^+ = A_1\tilde{\tau} [\tan \alpha] \) and \( a^- = A_1, \) while \( q = ny. \)

### ADDITIONAL SYMMETRIES

Apart from the translational symmetry, a 2D lattice has a rotational \( C_2 \) symmetry which is generated by the rotation for \( \pi \) around the axis perpendicular to layer. In addition, rhombic and rectangular lattices have vertical mirror and glide planes and also, in rhombic rectangular and hexagonal lattices the order of the rotational axis is four and six, respectively. However, atomic arrangements within the lattice unit cell may reduce the symmetry group to one of 80 diperiodic groups [11]. The additional symmetries, preserved after rolling up a layer into a NT may appear: two-fold rotational axis, mirror and glide planes. When combined with the roto-helical group \( L^{(1)} \) given by (3), they yield a line group which belongs to one of the remaining twelve families.

Rotation \( C_2 \) of a layer becomes horizontal two-fold axis, the \( U \)-axis, of the tube. Thus, whenever order of the principle axis of the layer is two, four, or six, symmetry of the NT is the fifth family line group \( TQ(f)D_n \) at least. Note that the higher order rotational symmetries of the layer do not give rise to the symmetry of NTs.

Vertical mirror (glide) plane is preserved in the NT only if the chiral vector is perpendicular onto it. When \( c \) is parallel to the plane, NT gets horizontal mirror (rotoreflective) plane. All these transformations can be combined (Tab. I) only with the roto-helical groups \( T(a)C_n \) or \( T_{2n}(a)C_n \) (i.e. \( \tilde{q} = 1,2 \)) of the achiral NTs.

Firstly, we consider rectangular lattices, \( \alpha = \pi/2 \) (i.e. \( Y = 0 \)). For irrational \( X = J \), we have \( w = y = 0 \), (then \( y = 1 \)) and \( x = 1 \), yielding \( \tilde{c}^+ = (1,0) \) and \( \tilde{c}^- = (0,1) \), with \( \tilde{q} = 1 \), i.e. the helical factor reduces to the pure translational group. For \( X \) rational, from Eq. (9) we get \( \tilde{q} = (\tilde{\tau}_1^2X + \tilde{\tau}_2^2X)/\text{GCD}(\tilde{n}_1, \tilde{\tau}_a, \tilde{\tau}_b) \). Thus, for \( X \neq 1 \), the same result as for \( X \) irrational is achieved, while in the case \( X = 1 \) (square lattice) additionally \( \tilde{q} = 2 \) is obtained for \( \tilde{c}^\pm = (\pm 1,1) \).

| Table I: Rolling-up correspondence of the line and diperiodic groups. For each family (column 1) of the linegroups all the different factorizations, roto-helical subgroup \( L^{(1)} \) and the isogonal point group \( P_q^d \) are given in the columns 2, 3 and 4 (for irrational \( Q \) in the families 1 and 5, \( q \) is infinite; \( T_q^d \) is glide plane bisecting vertical mirror planes or \( U \)-axes of \( P \)). The corresponding diperiodic groups enumerated according to Ref. 11 follow: for arbitrary chiral vector rolling gives either the first or fifth family line group; only for special chiral vector(s) \( a = \{(n,0), \} b = (0, n), c \in \{(n,0), (0, n)\}, d = \{(n,0), (0, n)\}, e \in \{(n,0), (-n, n)\}, f \in \{(n,0), (-n, n)\}, g \in \{(n,0), (n,0), (-n, n)\}, h \in \{(n,0), (-n, n), (-2n, 0), (-n, 2n), (2n, -n)\} the underlined groups (repeated after the corresponing vectors) give other line group families below. |
| --- | --- | --- | --- |
| Family | I | II | III |
| --- | --- | --- | --- |
| 1 | \( TQC_n \) | \( TQC_n \) | \( C_q \) |
| 2 | \( TQC_n \) | \( TQC_n \) | \( C_q \) |
| 3 | \( TQC_n \) | \( TQC_n \) | \( C_{nh} \) |
| 4 | \( TQC_n \) | \( TQC_n \) | \( C_{nh} \) |
| 5 | \( TQC_n \) | \( TQC_n \) | \( D_q \) |
| 6 | \( TQC_n \) | \( TQC_n \) | \( S_{nh} \) |
| 7 | \( TQC_n \) | \( TQC_n \) | \( S_{nh} \) |
| 8 | \( TQC_n \) | \( TQC_n \) | \( S_{nh} \) |
| 9 | \( TQC_n \) | \( TQC_n \) | \( S_{nh} \) |
| 10 | \( TQC_n \) | \( TQC_n \) | \( S_{nh} \) |
| 11 | \( TQC_n \) | \( TQC_n \) | \( S_{nh} \) |
| 12 | \( TQC_n \) | \( TQC_n \) | \( S_{nh} \) |
| 13 | \( TQC_n \) | \( TQC_n \) | \( S_{nh} \) |

Secondly, in the case of rhombic lattices \( A_1 = A_2 \) (\( X = 1 \)) for \( Y \) irrational, taking \( J = Y - 1 \), we have \( w = y = 1 \) and \( z = 0 \) (then \( z = 1 \)), yielding \( \tilde{c}^\pm = (\pm 1,1) \) with \( \tilde{q} = 2 \), i.e. \( L^{(1)} = T_{2n}(a/2)C_n \). For rational \( Y \), from (9) we get \( \tilde{q} = (n_1\tilde{n}_2^2)\tilde{\tau} + (n_2\tilde{n}_1^2)\tilde{\tau}/\text{GCD}(n_1\tilde{\tau}_1, n_2\tilde{\tau}_2) \), allowing the same \( \tilde{c}^\pm \) as for \( Y \) irrational. Only for \( Y = 0 \) and \( Y = 1 \) the additional pair, \( \tilde{c}^+ = (1,0) \) and \( \tilde{c}^- = (0,1) \), appear, giving \( \tilde{q} = 1 \) in a case of the square lattice, and again, \( \tilde{q} = 2 \) for the hexagonal lattice.

Finally, additional symmetries of the layer reduce the number of the different nanotubes. For the layers with the principle axis order \( n = 1,2,3,4,6 \), the effective interval of the chiral angle is \( 0,2\pi/n \), where \( n' = \text{LCM}(2, n) = 2, 2, 6, 4, 6 \), respectively. Further, vertical mirror plane of the layer intertwines the chiral vectors of the optically isomeric tubes, enabling to halve this range.
to $[0, \pi/n']$. However, if there is not such a plane, the optical isomer of tube $(n_1, n_2)$ is obtained from the layer reflected in the mirror plane (perpendicular to $A_1$) again as the tube $(n_1, n_2)$.

**DISCUSSION**

Full symmetries of NTs rolled up from arbitrary 2D layers for any chiral vector are described by line groups. Depending on 2D lattice and direction of chiral vector, NT may be incommensurate (line group from the first or fifth family) or commensurate. Without optical isomers (achiral) are NTs with pure transversal or zig-zag helical factors; they are always commensurate, and obtained for special chiral vectors from the rectangular and rhombic 2D lattice respectively, allowing mirror/glide planes. Present results agree with the known ones in the cases of hexagonal [1, 2] and rectangular [6] lattices.

The conserved quantum numbers related to the roto-helical symmetries of NTs are quasi-momenta [1, 2]: helical, $\tilde{k}$, from the helical Brillouin zone (HBZ) $(-\pi/f, \pi/f)$, and remaining (non-helical part) angular $\tilde{m}$, taking integer values from the interval $(-n/2, n/2)$. When $U$-axis, vertical or horizontal mirror/glide plane is a symmetry, the corresponding parity ($\Pi^U$, $\Pi^v$ and $\Pi^h$, taking values $+1$ and $-1$ for even and odd states) is conserved. More conventional quantum numbers for commensurate nanotubes are linear and total angular quasi-momenta, $\tilde{k}$ varying within Brillouin zone (BZ) $(-\pi/a, \pi/a)$ and $m$ (integers from $(-q/2, q/2)$), where $q$ is the order of the principle axis of the isogonal point group. However, $m$ is not conserved in the Umklapp processes.

These quantum numbers assigning energy bands $E_m^\kappa(\tilde{k})$ (or $E_m^\kappa(\kappa)$) of (quasi)particle spectra, correspond to irreducible representations of the NT’s line group; the dimension of representation is degeneracy of the band. Thus, for incommensurate NTs, degeneracy is either one or two, while for the commensurate also fourfold degeneracy is possible (families 9-13). In the families 2-5 and 9-13, z-reversing elements ($U$-axis, horizontal mirror/roto-reflectional plane) intertwine $\tilde{k}$ and $-\tilde{k}$ ($k$ and $-k$), causing at least twofold band degeneracy in the interior of the reduced HBZ $[0, \pi/f]$, with $0$ and $\pi/f$ being the only two points of degeneracy. However, this degeneracy is absent (but simultaneous intertwining of $\pm \tilde{m}$ and $\pm m$ caused by $U$-axis may preserve degeneracy for $\tilde{m} \neq 0, n/2$ and $m \neq 0, q/2$ in this points). Thus only these boundaries are special $\tilde{k}$- and $k$-points, where the bands joining and van Hove singularities appear. Let us mention that the NT’s electronic subsystem is in the nondegenerate state (excluding spin), as the Jahn-Teller theorem hold for the line groups [13].

The groups of the same family with same $n$ are isomorphic for any $Q$, and change of this continual parameter does not diminish symmetry. Accordingly, $Q$ should be varied in numerical relaxation. For the most studied NTs, carbon NTs, the graphene lattice is rhombic hexagonal, i.e. $X = 1$ and $Y = \frac{1}{2}$, giving commensurate NTs of fifth family, besides achiral zig-zag and armchair tubes of 13th family [2]. However, for the chiral tubes, the relaxation slightly changes helical axis, and there is no a priori physical reason for commensurability. Incommensurability affects the physical properties: quasi momentum fails to be conserved, and only the selection rules of the helical quantum numbers [1, 13] are applicable. This effect must be taken into account, particularly when external fields or mechanical influence [3] like twisting is studied.

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