Quantum mechanical calculation of electronic band structure of helically periodic systems: a case of nanotubes and nanohelicenes

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A method for obtaining electronic bands in the helical Brillouin zone based on the results of high-level quantum mechanical calculations using the CRYSTAL17 software package is considered. Using the example of a carbon nanotube of chirality (4,1), the preference of helical Brillouin zone in comparison with the translational Brillouin zone is shown. For nanohelicene, a system which is helically periodic only, bands of electronic states were obtained corresponding to the structure closest to the energy minimum. In addition, the evolution of the electronic bands of nanohelicene depending on torsion distortions is presented.

1. Introduction

Nanoobjects with a single helical axis of symmetry (hereinafter referred to as one-dimensional objects for short) in spiral topology possess unique properties. In addition to known biological DNA and RNA helices, there are other object: spiral stereoregular polymers, nanorods with spiral symmetry, nanotudes with different chirality, and other objects [1]. Theoretical studies of spiral nanostructures have certain peculiarities [2–4]. As opposed to the symmetry of triperiodic or biperiodic crystals, which is described by the space or layer groups, respectively, factorized by the translation subgroup of the crystal, one-dimensional objects should be described by spiral groups of symmetry (i.e., line groups). Line groups are factorized by a generalized translation subgroup, generated by a „generalized translation" $(C_Q|f)$. This operation, generated by the order Q screw axis, consists in rotation by „rotation angle" $\varphi = \frac{360°}{Q}$ and „shift" by f along the axis of symmetry. If Q is an irrational number, then the spiral system has no translation symmetry, but has spiral symmetry.

Thus, the application of the spiral group theory makes it possible to consider one-dimensional systems with or without translation symmetry. The authors of this paper have developed and applied to nanohelicenes [5] an original technique for the calculation of different properties (potential energy, Young modulus, bandgap) of one-dimensional systems without translation symmetry using interpolation of results obtained from calculations of one-dimensional systems with translation symmetry [6]. This gives the possibility to use modern high-level ab initio schemes of calculation based on the density functional method, in particular, its hybrid variants. The above-mentioned technique is also applicable to the calculation of electronic states of various one-dimensional systems, that makes it possible, for example, to proceed with the consideration of electronic properties of stereoregular polymers possessing spiral symmetry only.

Therefore, to describe spiral objects, concepts are introduced that naturally take into account the fact that the main parameter in the structure is the generalized translation, and not the translation. In particular, the concept of the „spiral Brillouin zone".

Zone patterns of electronic states in SBZ were obtained in a number of studies. Spiral stereoregular polymers were studied by the extended Hueckel method [7–12] and by the Hartree–Fock method [13,14]. Electronic bands of carbon nanotubes were calculated earlier on the basis of simplified calculation schemes without geometry optimization: DFTB (method of density functional tight binding) [4] and LACW (linear augmented cylindrical wave with the Slater local density functional) [15,16], DFT method in LDA (local electron density) approximation [17]. In [18–21] the DFT method is developed for studying spiral nanostructures, however, currently its applicability is limited by calculations of nanotubes and LDA approximation.

Thus, despite the developed theory of spiral bands, they were not obtained for the systems with spiral periodicity in high-level DFT-calculations with hybrid functionals, with geometry optimization and calculation of different physical properties, such as phonon spectra, magnetic structure (that requires calculations with spin polarization), etc.

This study presents a technique to obtain „spiral" electronic bands after transition to SBZ using results of high-level quantum-mechanical calculations by CRYSTAL17 software [22,23] by way of example of a carbon nanotube with a chirality of (4,1) and [1.1]helicene (see [5] for notations). It is worth noting, that [1.1]helicene (hereinafter —

nanohelicene) is a nanostructure that possesses only spiral periodicity [6]. We have compared electronic bands in TBZ and SBZ for a carbon nanotube with a chirality of (4,1) and used this example to show the preference of spiral classification for the analysis of electronic bands topology. It is worth noting, that, selectively, spiral bands (more specifically — the upper valent spiral band) obtained from the analysis of CRYSTAL17 calculation results were considered for some polymers [11,12]. However, the algorithm presented in this study makes it possible to automate the process of obtaining all electronic bands in SBZ, providing the general pattern of electronic states in their spiral classification.

2. Structure of spiral groups

Let us take a brief look at key points of the theory of spiral groups of symmetry, that are needed for understanding the results of this study. A rigorous description can be found in [4].

As it was already mentioned above, the essential difference of spiral groups of symmetry from single-periodic groups consists in the use of the generalized translation $Z = (X|f)$, where X is either C_Q rotation about the Oz axis, or σ_V reflection in the plane that contains Oz axis, and f is shift along the Oz axis. The action of Z operation translates one „monomer" (an atomic fragment of minimum size, that does not change when the generalized translation is used) to the neighboring one, and all possible powers of this operation, Z^n, compose an infinite cyclic group $\mathbf{Z}$. If $X = C_Q$, then group $\mathbf{Z}$ is composed of $(C_Q|f)^n$ operations. The C_Q defines rotation of monomer about Oz axis by an angle of

$$\varphi = \frac{360°}{Q}, \quad Q \geq 1. \tag{1}$$

If there is a translational periodicity, it means, that in the group $\mathbf{Z}$ there are operations of $(I|a)$ type, where I is a single operation, and a is a period of translation. Otherwise speaking, there is a subgroup $\mathbf{T}$ of pure translations in $\mathbf{Z}$. It means, that there is a q, that

$$(X|f)^q = (X^q|qf) = (I|a). \tag{2}$$

That is the period a can be expressed through f as follows

$$a = qf. \tag{3}$$

For the $(C_Q|f)$ operation the condition of $X^q = I$ results in that the order of the screw axis, Q, should be a rational number

$$Q = \frac{q}{r}, \quad q \geq r, \tag{4}$$

q and r are coprime integers.

The angle of monomer rotation in case of rational Q is:

$$\varphi = \frac{r \cdot 360°}{q}. \tag{5}$$

If symmetry of a one-dimensional system is described by a group with rational Q, then this system is called „commensurate" [4] and is translationally periodic in addition to spiral periodicity. If Q is an irrational number, the system is called „incommensurate ", because there is no translational periodicity and the system has spiral periodicity only.

Spiral group $\mathbf{L}$, that describes the symmetry of one-dimensional system, is factorized by group $\mathbf{Z}$ of generalized translations

$$\mathbf{L} = \mathbf{Z}\mathbf{P}, \tag{6}$$

where $\mathbf{P}$ — axial point group symmetry, reflecting additional symmetry of the monomer shared with operations of group $\mathbf{Z}$. This factorization is called „spiral" (or „polymer"). Depending on $\mathbf{P}$, thirteen „families" of spiral groups are possible, however „incommensurate" systems can only belong to the first or the fifth families.

The first family is composed of groups with $\mathbf{P} = \mathbf{C}_n$ — the group of rotations about Oz axis. In case of systems considered in this study, the axis order is equal to one, therefore $\mathbf{P} = \mathbf{C}_1$ and in this case $\mathbf{L} = \mathbf{Z} \times \mathbf{C}_1$ coincides with group $\mathbf{Z}$.

The fifth family is composed of groups with $\mathbf{P} = \mathbf{D}_n$. As compared with group $\mathbf{C}_n$, group $\mathbf{D}_n$ has rotation operations U by 180° about the axes normal to the Oz main axis. For the systems considered in this study: $\mathbf{P} = \mathbf{D}_1$, therefore $\mathbf{L} = \mathbf{Z} \wedge \mathbf{D}_1$.

If Q is a rational number, then, in addition to spiral factorization, the spiral group also allows „translational" factorization by subgroup $\mathbf{T}$. Group $\mathbf{L}$ for this factorization can be expanded in adjacent classes by the subgroup $\mathbf{T}$ as follows:

$$\mathbf{L} = \sum_{j=1}^{q} \left(C_q^j \middle| \left\{ \frac{jp}{q} \right\} a \right) \mathbf{T}(a) \tag{7}$$

— the first family,

$$\mathbf{L} = \sum_{j=1}^{q} \left[\left(C_q^j \middle| \left\{ \frac{jp}{q} \right\} a \right) + U \left(C_q^j \middle| \left\{ \frac{jp}{q} \right\} a \right) \right] \mathbf{T}(a) \tag{8}$$

— the fifth family.

Here C_q^j — rotation by angle $\varphi_j = j \frac{360°}{q}$; $\left\{ \frac{jp}{q} \right\} a$ — translation to fractional part of jp/q number multiplied by a period of a. Parameter $p < q$, that is present in the translational factorization, sets the translation to a fraction of period when rotating by the minimum angle of $\varphi_1 = 360°/q$. For the systems considered in this study: $\mathbf{C}_n = \mathbf{C}_1$, therefore p and q are coprime numbers.

Elements $(C_q^j|jp/qa)$ do not for a group, however, rotations C_q^j form the isogonal group $\mathbf{C}_q$. The translational factorization makes it possible to use crystallographic notations of spiral groups: Lq_p for the first family and Lq_p2 for the fifth family.

Thus, with a rational Q two factorizations are possible: spiral one, defined by parameters (q, r, f), and translational one, defined by parameters (q, p, a). Parameter q is the same for both factorizations, f and a are related to each

other by equation (3), and parameters r and p for the systems considered in this study can be expressed through each other according to the following formula:

$$rp \pm 1 = ql, \tag{9}$$

where l is a positive integer number.

In [6] we have proposed an algorithm that makes it possible to use CRYSTAL17 software package for quantum-mechanical study of spiral periodic systems [22,23]. This software was developed for calculations in the translational factorization. Optimized atomic and electronic structures of spiral periodic systems with irrational Q are obtained by interpolating the results for translationally periodic systems with rational Q, which are taken from an interval, that also allows plotting the curve of dependence of energy versus torsional stresses. The control of computational resources is defined by setting r_{max}, and values of Q in the interval should be selected in such a way, as to ensure $r \leq r_{max}$.

3. Irreducible representations of spiral groups

Since group $\mathbf{Z}$ is a cyclic Abelian group (with generator $Z = (C_Q|f)$), its irreducible representations (IR) are expressed in a simple form

$$A_{\tilde{k}}(Z) = e^{i\tilde{k}f}, \quad \tilde{k} \in \left(-\frac{\pi}{f}, \frac{\pi}{f}\right]. \tag{10}$$

Interval $(-\pi/f, \pi/f]$ is called the „spiral Brillouin zone" (or „Jones zone"). Parameter $\tilde{k}$ can be defined as a „spiral" wave vector.

IRs of the finite cyclic Abelian group $\mathbf{C}_n$ (with generator C_n) are defined as follows

$$A_{\tilde{m}}(C_n) = e^{i\tilde{m}2\pi/n}, \quad \tilde{m} \in \left(-\frac{\pi}{2}, \frac{\pi}{2}\right]. \tag{11}$$

Thus, IRs of spiral groups of the first family are expressed as products of IRs of groups $\mathbf{Z}$ and $\mathbf{C}_n$ and are defined by two quantum numbers $\tilde{k}$ and $\tilde{m}$. Since in this study we consider systems with $n = 1$, it can be assumed that $\tilde{m} = 0$.

IRs for the fifth family are additionally defined by „parity" Π_U. In case of singular points defined by values of $\tilde{k} = 0, \frac{\pi}{f}$ and $\tilde{m} = 0, \frac{n}{2}$, IRs will be one-dimensional and expressed through products of IRs for generators $(10), (11)$ and Π_U. Other IRs are two-dimensional (see [4]) and do not arise in this study because we only consider the case of $\tilde{m} = 0$.

Relationships $(10), (11)$ make it possible to determine IRs for spiral periodic systems, including those without transla-tional periodicity (irrational values of Q). If the symmetry of a system is defined by a rational Q, then it is possible to introduce IRs that are defined by more traditional quantum numbers k and m based on representations of the subgroup of translations $\mathbf{T}$ and isogonal group $\mathbf{C}_q$:

$$A_k(I|a) = e^{ika}, \quad k \in \left(-\frac{\pi}{a}, \frac{\pi}{a}\right], \tag{12}$$

$$A_m(C_q) = e^{im2\pi/q}, \quad m \in \left(-\frac{\pi}{2}, \frac{\pi}{2}\right]. \tag{13}$$

Interval $(-\pi/a, \pi/a]$ is a one-dimensional Brillouin zone in the usual sense, and k is a „translational" wave vector. Since $\mathbf{C}_q$ is not a subgroup of spiral group $\mathbf{L}$, TRs of its generators are defined by more complex expressions

$$A_{k,m}(I|a) = e^{ika}, \tag{14}$$

$$A_{k,m}\left(C_q^1 \middle| \left\{\frac{p}{q}\right\}a\right) = e^{ikap/q} \cdot e^{im2\pi/q}. \tag{15}$$

Since pairs $(\tilde{k}, \tilde{m})$, and (k, m) define representations for the same group, it is possible to transit from one pair to another and the reverse. In this study we use transition in one direction only, i.e., from translational to spiral factorization:

$$(\tilde{k}, \tilde{m}) = \left(k + rm\frac{2\pi}{a} + Kq\frac{2\pi}{a}, m + M\right). \tag{16}$$

Expression (16) is written for the case of $n = 1$ and makes it possible to obtain $(\tilde{k}, \tilde{m})$ values at set (k, m). Integers K and M are determined from the requirement that $(\tilde{k}, \tilde{m})$ are within the intervals defined in (10) and (11). Also, it is worth noting, that the condition of $n = 1$ automatically sets $\tilde{m} = 0$.

4. Technique to obtain electronic spiral bands

Symmetry is taken into account by CRYSTAL17 software in the translational factorization. It means, that solving the Hartree–Fock or Kohn–Sham equations gives one-electron wave function $\chi_{kmi}(x, y, z)$ and their energies ε_{kmi} are classified by quantum numbers (k, m), and i index allows distinguishing the states with an identical set of k and m.

Grouping one-electron energies as functions of k, $\varepsilon_{mi}(k)$ allows obtaining electronic state bands in TBZ, which topology interpretation makes it possible to predict some or other electronic properties of the system.

However, since k is determined via the translational period a, it becomes difficult to interpret energy bands for spiral periodic systems (even with rational Q), and in case of incommensurate systems they become simply inaccessible. Therefore, a need arises to introduce „spiral" bands of one-electron energies, i.e., reclassify $\varepsilon_{mi}(k)$ values into spiral factorization and obtain continuous functions $\varepsilon_{\tilde{m}j}(\tilde{k})$ in general case, and $\varepsilon_j(\tilde{k})$ for the systems considered in this study. Thus, to obtain spiral bands, it is necessary to translate the $\varepsilon_{mi}(k)$ values obtained in CRYSTAL17 as a result of solving the electronic problem (Hartree–Fock or Kohn–Sham) to $\varepsilon_j(\tilde{k})$.

According to (16), to determine $\tilde{k}$ it is necessary to know a pair of (k, m) for each ε. Accordingly, the algorithm of actions to obtain $\varepsilon_j(\tilde{k})$ functions consists in calculating in the CRYSTAL17 software an electronic

structure (with optimized geometry) in translational factorization, outputting to file the ε values and (k, m) indices for them, and further reclassifying by formula (16). The last task required a separate program to be written to automate the process, because even for relatively simple systems the number of values of one-electron energies ε may be hundreds or thousands. Unfortunately, though, the derivation of ε distribution over k in CRYSTAL17 is implemented correctly, the procedure to derive distributions of ε over m gives incorrect values (though the quantum-mechanical calculation itself is correct). To determine m, in this study we used another approach based on the Wigner's theorem (see [24] for its application in quantum-mechanical calculations of solid states).

The Wigner's theorem makes it possible to use the fact that eigenvectors of the $\hat{F}$ operator (Hartree–Fock or Kohn–Sham), defined in a symmetrized basis of crystalline orbitals, are transformed by IR of the symmetry group of the physical system. Since for the first family of spiral groups all IRs are one-dimensional, then $\mathbb{D}(g)$ matrices of $\hat{D}(g)$ operators corresponding to operations of g symmetry in the space of one-electron states will be diagonalized simultaneously with the energy operator. In case of the first family and $\mathbf{C}_1$ symmetry of monomer, g operations are $(C_q^j | jp/qa)$ from equation (7).

Eigenvectors of the $\hat{F}$ operator form the $\mathbb{C}$ matrix that diagonalize the matrix of energy operator, $\mathbb{F}$:

$$\mathscr{E} = \mathbb{C}^{-1}\mathbb{F}C. \tag{17}$$

And simultaneously $\mathbb{C}$ diagonalize $\mathbb{D}(g)$ matrices:

$$\mathscr{D}(g) = \mathbb{C}^{-1}\mathbb{D}(g)\mathbb{C}. \tag{18}$$

The $\mathscr{D}(g)$ diagonal matrix contains in its main diagonal a set of IR numbers corresponding to g operation. Comparison of these numbers with values obtained by formula (15) makes it possible to precisely identify m, use (16) to obtain values of $\tilde{k}$ and build up spiral bands of electronic states.

The process of building $\mathbb{D}(g)$ matrices, that are matrices of regular representation in the systems under study, appeared to be the most complex. Dimension of $\mathbb{D}(g)$ is equal to the number of all Bloch sums of atomic basic functions per one translational cell.

Coefficients of eigenvectors expansion in the basis of Bloch functions can be derived in CRYSTAL17 using the CRYAPI_OUT option. Here the main problem is to build up the $\mathbb{D}(g)$ matrices of regular representation exactly in the implementation that is used in CRYSTAL17 software. The procedure to build up $\mathbb{D}(g)$ matrices in CRYSTAL17 is described in detail in [25] (see formulae $(21)-(24)$). Currently we have implemented the procedure to build up a regular representation of $\mathbb{D}(g)$ for atomic s- and p-functions, therefore, it is limited by elements of the first and the second periods.

Calculations were carried out in CRYSTAL17 software. Geometry was optimized by the DFT method with PBE0 hybrid functional [27] in a split-valence basis

with polarizing d-functions pob-TZVP [28]. The electronic structure was calculated to obtain electronic state bands in SBZ using the same PBE0 functional in the basis formed from pob-TZVP by the removal of polarizing d-functions. We have verified that the atomic basis of d-orbital has almost no effect on the electronic structure.

5. Results

Spiral symmetry of one-dimensional systems defines the features of their electronic energy bands. The topology of electronic energy bands in one-dimensional systems has its specifics and is described in detail by way of example of carbon single-wall nanotubes with different diameters. In [4] it is shown, that spiral electronic bands can be introduced instead of the difficult-to-interpret pattern of translational bands. The application of the above-discussed „non-crystallographic" factorization (6) allows transiting to spiral electronic bands. At the same time, as noted in [4], translational and spiral bands correspond to different classifications of the same electronic states of a one-dimensional system, and, therefore, the same set of eigenvalues and, as a consequence, the same nature of the system (metal, semiconductor), because the bandgap remains unchanged with changes in the classification of electronic states.

As an illustration of the presented technique to obtain the spiral band structure of electronic states, let us consider spiral bands of a chiral carbon nanotube (4,1), for comparison with earlier results [16]. For the carbon nanotube with a chirality of (n_1, n_2) the following relationships are true, that allows obtaining of parameters q and r (at $n_1 = 4$, $n_2 = 1$):

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 \tag{19}$$

— folding vector,

$$\mathbf{T} = t_1\mathbf{a}_1 + t_2\mathbf{a}_2 \tag{20}$$

— translation vector,

$$\frac{t_1}{t_2} = -\frac{2n_2 + n_1}{2n_1 + n_2} = -\frac{2}{3}, \tag{21}$$

$$q = \det\begin{pmatrix} 4 & 1 \\ -2 & 3 \end{pmatrix} = 14, \tag{22}$$

$$n_1h_2 - n_2h_1 = 4h_2 - h_1 = 1, \quad h_1 = 3, \quad h_2 = 1, \tag{23}$$

$$r = h_1t_2 - h_2t_1 = 11. \tag{24}$$

Here $\mathbf{a}_1$ and $\mathbf{a}_2$ are translation vectors of the graphene layer with an angle of $60°$ between them, and chiral vector $h = h_1\mathbf{a}_1 + h_2\mathbf{a}_2$ [26]. Thus, for tube (4,1) with a symmetry of the fifth family of spiral groups, the screw axis has an order of $Q = 14/11$. Parameter $p = 5$ (see (9)), therefore in the crystallographic notation symmetry of nanotube (4,1) will be denoted as $L14_52$.

Each wave number k in the translation band has $q = 14$ corresponding values of $\tilde{k}$ vector in the spiral band, while
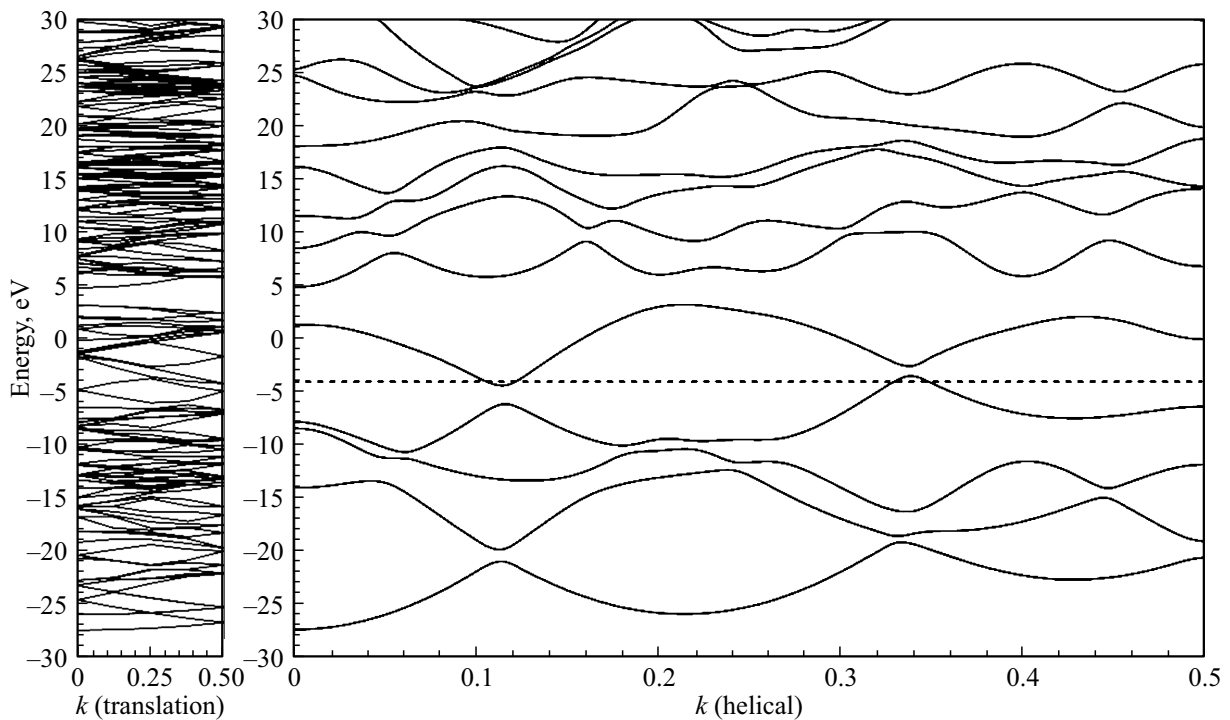
Figure 1. Electronic energy bands in TBZ (left) and SBZ (right) of a carbon nanotube (4,1). Values of k and $\tilde{k}$ vectors are presented in fractions of translation vector of the corresponding reciprocal lattice. Fermi energy is shown by a dashed line in SBZ.

Correspondence of wave vector values in two factorizations *

k, TBZ	$\tilde{k}$, SBZ
0	0, 1/14, 2/14, 3/14, 4/14, 5/14, 7/14 ($=0.5$)
0.5	1/28, 3/28, 5/28, 7/28 ($=0.25$), 9/28, 11/28, 13/28
0.25	1/56, 3/56, 7/56, 9/56, 11/56, 13/56, 17/56

N o t e. * Values are presented in fractions of translation vector of the corresponding reciprocal lattice.

the total number of translation bands is defined by the dimension of the selected atomic basis. For example, for the upper valent translational band we get $28 \cdot 2 = 56$, where 28 — number of carbon atoms in a translational periodic cell, and 2 derives from the fact that valent electrons are at $2s$- and $2p$-orbitals. It follows from this that 56 occupied translational bands have corresponding $56/14 = 4$ occupied spiral bands. The correspondence of wave vector values can be easily determined from the table.

This correspondence can be also determined using genkpt software [29] that links the points of the narrowed Brillouin zone (in this case it is TBZ) and the initial Brillouin zone (in this case it is SBZ), showing certain analogy between the idea of a spiral band and idea of a „supercell". The above-mentioned software is intended to determine the correspondence between points in the Brillouin zone in the method of SUPERCELL-ZONE FOLDING (expanded cell in a direct lattice — the narrowed Brillouin zone in a reciprocal lattice); see [29] for the detailed description of

this method and genkpt software. It can be seen in Fig. 1, that the pattern of translational bands gives an electronic structure of a tube as that of metal, while in the pattern of spiral bands the situation is more complex. The upper spiral valent band is partly located above the Fermi level, while the lower conduction band is partly located below the Fermi level. However, the system as a whole is a metal, because the above-mentioned parts of bands contain an equal number of states. This unusual feature of spiral bands was obtained earlier for the tube in question when calculated by the LACW method [16].

The spiral bands of a nanotube (4,1) shown in Fig. 1 are mainly of methodic character; this system was not considered as having translational periodicity, therefore it became possible to consider it in terms of two different factorizations. At the same time it is shown, that even in these examples the spiral factorization is considerably advantageous due to the better interpretation of bands (Fig. 1).

This advantage fully shows its worth when studying the band pattern for „incommensurate" systems that have spiral periodicity only. Here we present spiral electronic bands of a nanohelicene, that, as it is shown in [6], is a system having spiral periodicity only. Moreover, the use of spiral factorization makes it possible to consider the order of screw axis Q as a parameter, that changes continuously under torsion distortion. Accordingly, the pattern of spiral bands under torsion distortion changes continuously as well.

In this context nanohelicene is understood as a one-dimensional structure, that can be considered as a gener-
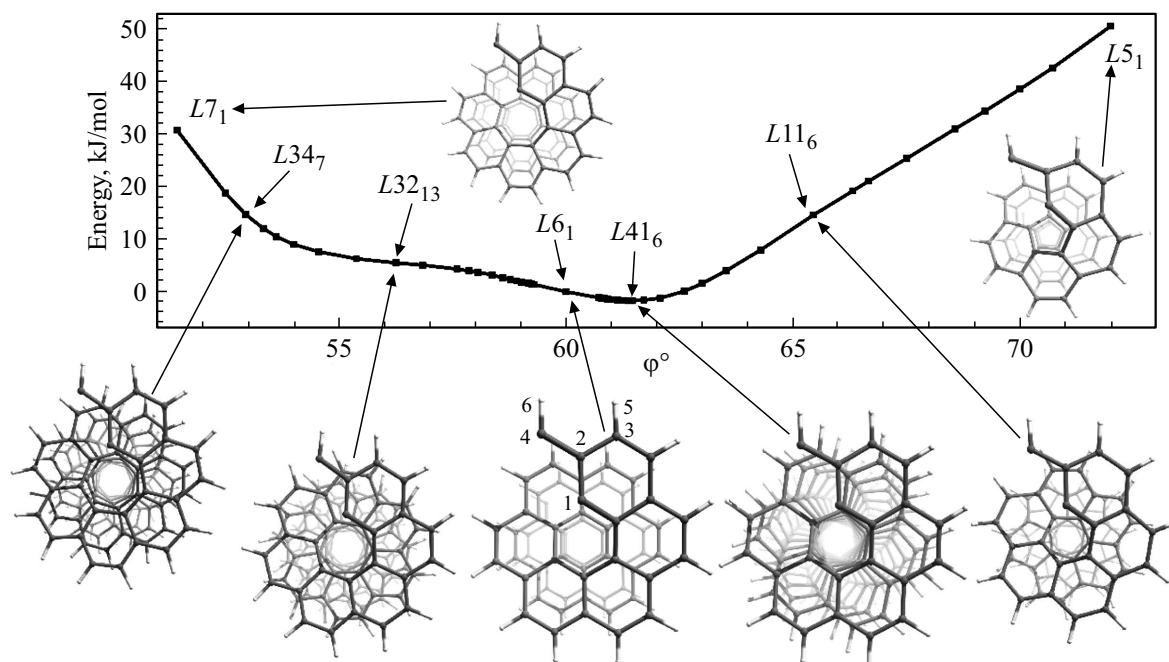
Figure 2. $E(\varphi)$ dependence in the interval of $\varphi \in [51.43°, 72°]$. Plan view (along Oz axis) of the atomic structure of nanohelicene, grey atoms $(1, 2, 3, 4)$ — carbon, white atoms $(5, 6)$ — hydrogen. For the structure *with* symmetry $L6_1$ numbering of monomer atoms is shown.
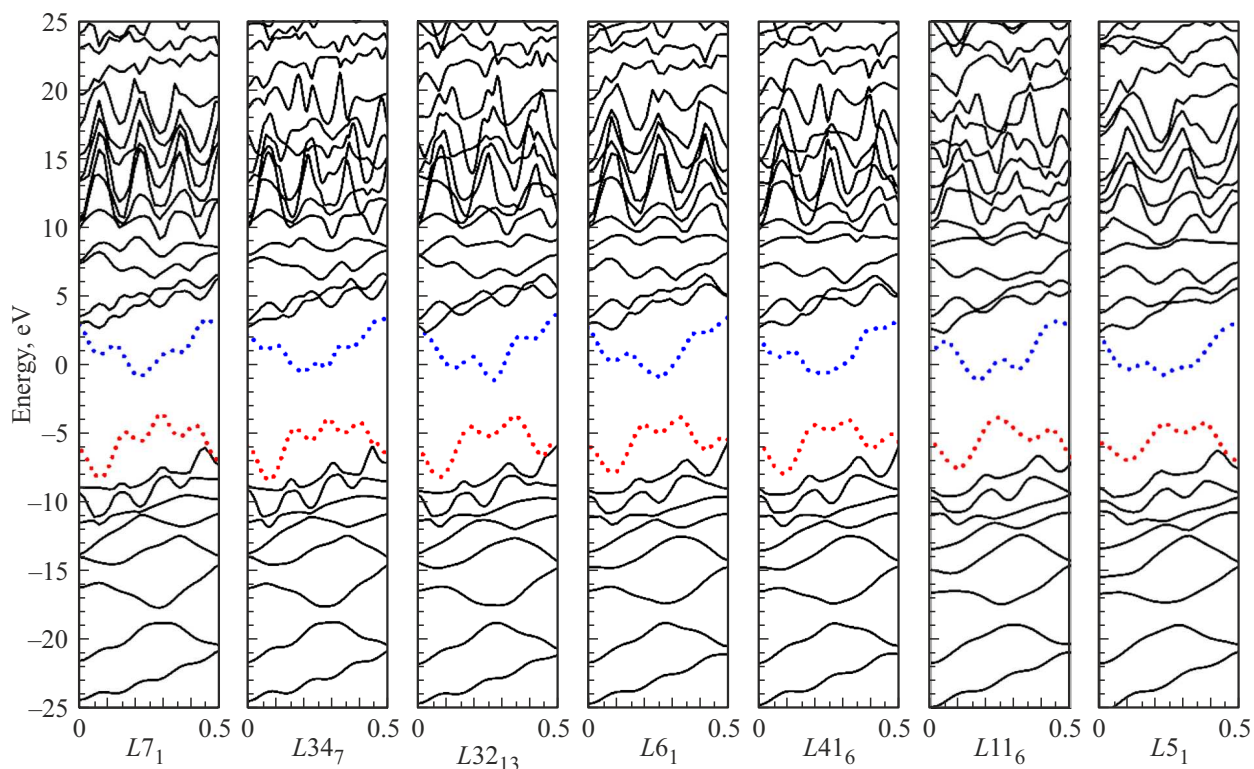

Figure 3. Electronic state bands of nanohelicene in SBZ. The symmetry corresponds to points on the torsion curve $E(\varphi)$ in Fig. 2. The upper valent band is shown by a red dashed line, the lower conduction band is shown by a blue dashed line.

alization of molecular helicenes [30], that consists in the extension to infinity of the adjoining π-system by screwing about the screw axis. Previously we have shown [6], that these systems are spiral periodic, minimum energy should be achieved at irrational value of Q. It is convenient to define the $E(\varphi)$ energy per one monomer in some fixed spiral symmetry. Here the energy of monomer at $\varphi = 60°$ is assumed as a zero value.

The use of the algorithm presented in [6] makes it possible to derive the dependence of $E(\varphi)$ energy of monomer on the rotation angle (see Fig. 2) and determine the value of irrational Q that corresponds to the minimum energy by means of interpolation between neighboring rational values of Q [6]. Plan view of the atomic structure of nanohelicene at selective values of φ, as well as corresponding notation of the symmetry group are shown in Fig. 2. For the structure with symmetry $L6_1$ figures additionally indicate the atoms that compose the monomer: thus, the monomer of the nanohelicene has the following composition: C_4H_2.

Fig. 3 illustrates evolution of band patterns in SBZ in the interval of φ angles shown in Fig. 2. In each of the band patterns nine valence bands are kept because the monomer has 18 valent electrons. The presence of a bandgap matches the fact that the nanohelicene is a semiconductor in the entire considered interval of φ angles, though the value of the bandgap changes when φ is varied.

In the presented here results, the structure with symmetry $L41_6$ is the most close in terms of energy to the point of $E(\varphi)$ minimum, accordingly, the band pattern of electronic states at symmetry $L41_6$ in Fig. 3 is the most close to the pattern that corresponds to the $E(\varphi)$ minimum. It means, that changes in the band patterns for other points of the $E(\varphi)$ curve can be considered as changes attributable to torsion distortions of the nanohelicene's atomic structure.

As can be seen from Fig. 3, torsion distortions of the nanohelicene's atomic structure in both directions: „screw-in" (i.e., increase in φ) and „screw-out" (decrease in φ) leave unchanged the total topology of the electronic state bond structure in SBZ. Only partial changes are observed that manifest smoothly during transition from one boundary of the studied interval of φ angles to another. This is a reflection of the fact that the atomic structure of the nanohelicene is kept in the entire studied interval of angles, allowing quite free sliding of spiral turns in relation to each other similar to layers of graphite.

6. Conclusion

A technique is presented to obtain bands of electronic states in the spiral Brillouin zone from quantum-mechanical calculations performed in translational factorization of spiral group of symmetry of one-dimensional nanostructures. By way of example of a carbon nanotube with a chirality of (4,1) the preference of spiral classification for the analysis of electronic bands topology is shown.

The band pattern of electronic states in SBZ is built for a nanohelicene having spiral periodicity only, which matches well in terms of energies the minimum on the curve of energy vs rotation angle, $E(\varphi)$. Building up band patterns for other points on $E(\varphi)$ makes it possible to consider the evolution of electronic structure at torsion distortions. It is shown for the nanohelicene, that „screwing-in" and „screwing-out" torsion distortions cause little changes in the electronic band structure in SBZ, that corresponds to keeping the atomic structure in the entire interval of torsion distortions.

Conflict of interest

The authors declare that they have no conflict of interest.

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