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Generalized Bloch states and potentials of nanotubes and other quasi-1D systems

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Abstract

Bases of invariant and covariant functions for the systems with all possible line group symmetries are found. This is used to generalize the Bloch theorem to the full line group symmetry and to derive the most general forms of the emitting fields. Applications in the physics of nanotubes, polymers and other quasi-1D structures are discussed.

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1. Introduction

Discovery of carbon nanotubes [1] and, later on, transition metal dichacogenide [2] and other kinds of nanotubes [3] as well as zinc oxide nanowires and nanosprings [4], all of which may have high-order principle axis, helical, but not always translational periodicity [5], combined with several types of parities, stressed out necessity of application of line groups in nanophysics [6].

Line groups [7] describe symmetries of the systems with periodicity along a single direction (the z-axis by convention). The periodicity can be simultaneously helical and translational (including trivially helical, i.e. just translational) or only helical. The latter possibility is a consequence of the lack of the crystallographic restrictions on the order of the principle axis where a screw-axis may involve rotations for an angle incommensurate to 2π. Therefore, in contrast to the finite number of the diperiodic and space groups, there are infinitely many line groups. Some of the subgroups of the diperiodic and space groups describe symmetry of the quasi-1D systems, i.e. they are line groups. There are 80 such subgroups and they are also called *rod groups* [8].

Quantum-mechanical approach is indispensable in interpretation and prediction of the most remarkable properties of the nano-systems. Usage of the symmetry adapted basis (SAB) of the single particle quantum state space $\mathcal{L}(\mathbb{R}^3)$ is necessary in any quantum-mechanical study. This paper addresses the problem of finding SAB for all possible quasi-1D systems.

Namely, for the most general line group symmetry, the functions which make the symmetry adapted basis are found.

Transformation ℓ of the line group $\boldsymbol{L}$ acts on a function $f(\boldsymbol{r})$ according to the law:

$$\ell F(\boldsymbol{r}) \stackrel{\text{def}}{=} F(\ell^{-1}\boldsymbol{r}), \tag{1}$$

and invariant functions, which satisfy

$$H(\ell^{-1}\boldsymbol{r}) = H(\boldsymbol{r}), \qquad \forall \ell \in \boldsymbol{L}, \tag{2}$$

form a subspace of $\mathcal{L}(\mathbb{R}^3)$. A basis of this subspace will be explicitly found. Covariant functions, i.e. the functions transforming according to the nonsymmetric irreducible representations, will be also discussed, and their general form (which enables construction of the SAB for arbitrary quasi-1D crystal) will be derived.

This group theoretical result has many applications in solving physical problems. Firstly, it enables generalization of the Bloch theorem: from the translational to the full line group symmetry of the quasi-1D system. Moreover, such a generalization refers also to the non-Abelian groups, as well as to the incommensurate quasi-1D crystals (with helical but not translational periodicity). Further, this way imposed restrictions onto the form of the e.g., electronic eigenfunctions, besides giving deep insight into the physical properties of the considered physical systems through the direct implementation of the selection rules, may significantly improve quality and efficiency of the numerical (e.g. density functional) calculations (as the basis set of functions used is optimal). Finally, potential produced by the system (nanotube, for instance) is to be invariant under its symmetry group which means that this potential can be expanded over the basis of invariants, revealing profound interrelation of the symmetry and the dynamics of the system.

After a brief remainder on the line group structure (section 2), the invariant functions are derived (section 3). These results are used to generalize the Bloch form of the wavefunctions to the helical systems (section 4). Finally, the obtained results are applied to nanotubes: their electronic eigenfunction forms and potentials formed by them are discussed (section 5).

2. Line groups structure and helical coordinates

All line groups are products [7] $\boldsymbol{ZP}$ of an infinite cyclic subgroup $\boldsymbol{Z}$, called the group of *generalized translations* with an axial point group $\boldsymbol{P}$. Possible types of generalized translational groups are helical (or the screw-axis) $\boldsymbol{T}_{Q'}(f)$ and glide-plane group $\boldsymbol{T}'(a/2)$, generated by the elements (Koster–Seitz notation) $(C_{Q'}|f)$ and $(\sigma_{\mathrm{v}}|a/2)$, respectively. Here, σ_{v} is a mirror plane containing the z-axis, while $C_{Q'}$ is the rotation around the z-axis for $2\pi/Q'$. It should be stressed out that Q' may be any real number, but for uniqueness we assume $Q' \geqslant 1$. Pure translational group $\boldsymbol{T}(a)$ (generated by $(I|a)$) is a special case of the screw-axis with trivial rotational part, $Q' = 1$. Only for Q' rational, $Q' = q'/r'$ (q' and r' integers), the screw-axis (denoted then as $\boldsymbol{T}^{r'}_{q'}(f)$) has a subgroup of pure translations $\boldsymbol{T}(q'f)$, as $(C_{Q'}|f)^{q'} = \left(C^{r'q'}_{q'}\middle|q'f\right) = (I|q'f)$.

Axial point groups are classified into the seven families, each of them parameterized by the order n of the principle rotational axis: $\boldsymbol{C}_n$, $\boldsymbol{S}_{2n}$, $\boldsymbol{C}_{n\mathrm{h}}$, $\boldsymbol{D}_n$, $\boldsymbol{C}_{n\mathrm{v}}$, $\boldsymbol{D}_{n\mathrm{d}}$ and $\boldsymbol{D}_{n\mathrm{h}}$. The products are always weak-direct, as $\boldsymbol{Z} \cap \boldsymbol{P} = (I|0)$ (identity element of the group), and in some cases when one or both factors are invariant, it is a semidirect or a direct product. However, any combination is not a group, but only those which satisfy the compatibility condition $\boldsymbol{ZP} = \boldsymbol{PZ}$ [9]. This effectively restricts the screw-axis compatible with the vertical and horizontal mirror parities to the achiral cases: pure translational $\boldsymbol{T}(f)$ and zig-zag $\boldsymbol{T}^1_2(f)$ (we call *chiral* the compound giving non-equivalent structure under spatial inversion, i.e. the

Table 1. Harmonics of the line groups. For each family (column 1) its factorization (used in the calculations) and the first family subgroup $\boldsymbol{L}^{(1)}$ with the remaining generators are given (column 2); the U-axis coincides with the x-axis, σ_{v} is the xy-plane, and U' bisects vertical mirror planes. Bases of harmonics are given in the last column. They are expressed through the chiral, translational or zig-zag (C, T, Z) harmonics, and in the explicit form below. For the first family K and M take all integer values, for families 2–4 and 5–8 K and M are respectively non-negative (for family 5 instead of M alternatively K may be taken non-negative), while for families 9–13 both M and K are non-negative.

Family $\boldsymbol{L}^{(1)}$, generators	H_K^M
1 $\boldsymbol{T}_q^r(f)\boldsymbol{C}_n$	$S_K^M = F^{nM}_{(-Mr+K\tilde{q})/a}$
$\boldsymbol{T}_q^r(f)\boldsymbol{C}_n$	$\mathrm{e}^{\mathrm{i}nM\varphi}\mathrm{e}^{\mathrm{i}2\pi(K\tilde{q}-Mr)z/a}$
2 $\boldsymbol{T}(a)\boldsymbol{S}_{2n}$	$\frac{1}{2}T_K^M + \frac{1}{2}(-)^M T_{-K}^M$
$\boldsymbol{T}(a)\boldsymbol{C}_n, C_{2n}\sigma_{\mathrm{h}}$	M even: $\mathrm{e}^{\mathrm{i}nM\varphi}\cos 2\pi Kz/a$
	M odd: $\mathrm{e}^{\mathrm{i}nM\varphi}\sin 2\pi Kz/a$
3 $\boldsymbol{T}(a)\boldsymbol{C}_{nh}$	$\frac{1}{2}T_K^M + \frac{1}{2}T_{-K}^M$
$\boldsymbol{T}(a)\boldsymbol{C}_n, \sigma_{\mathrm{h}}$	$\mathrm{e}^{\mathrm{i}nM\varphi}\cos 2\pi Kz/a$
4 $\boldsymbol{T}^1_{2n}(a/2)\boldsymbol{C}_{nh}$	$\frac{1}{2}Z_K^M + \frac{1}{2}Z_{M-K}^M$
$\boldsymbol{T}^1_{2n}(a/2)\boldsymbol{C}_n, \sigma_{\mathrm{h}}$	$\mathrm{e}^{\mathrm{i}nM\varphi}\cos 2\pi(2K-M)z/a$
5 $\boldsymbol{T}_q^r(f)\boldsymbol{D}_n$	$\frac{1}{2}S_K^M + \frac{1}{2}S_{-K}^M$
$\boldsymbol{T}_q^r(f)\boldsymbol{C}_n, U$	$\cos(nM\varphi + 2\pi(K\tilde{q}-Mr)z/a)$
6 $\boldsymbol{T}(a)\boldsymbol{C}_{nv}$	$\frac{1}{2}T_K^M + \frac{1}{2}T_K^{-M}$
$\boldsymbol{T}(a)\boldsymbol{C}_n, \sigma_{\mathrm{v}}$	$\cos nM\varphi\,\mathrm{e}^{\mathrm{i}2\pi Kz/a}$
7 $\boldsymbol{T}_c(a/2)\boldsymbol{C}_n$	$\frac{1}{2}T_K^M + \frac{1}{2}(-)^K T_K^{-M}$
$\boldsymbol{T}(a)\boldsymbol{C}_n, (\sigma_{\mathrm{v}}\vert\frac{1}{2})$	K even: $\cos nM\varphi\,\mathrm{e}^{\mathrm{i}2\pi Kz/a}$
	K odd: $\sin nM\varphi\,\mathrm{e}^{\mathrm{i}2\pi Kz/a}$
8 $\boldsymbol{T}^1_{2n}(a/2)\boldsymbol{C}_{nv}$	$\frac{1}{2}Z_K^M + \frac{1}{2}Z_{K-M}^{-M}$
$\boldsymbol{T}^1_{2n}(a/2)\boldsymbol{C}_n, \sigma_{\mathrm{v}}$	$\cos nM\varphi\,\mathrm{e}^{\mathrm{i}2\pi(2K-M)z/a}$
9 $\boldsymbol{T}(a)\boldsymbol{D}_{nd}$	$\frac{1}{4}T_K^M + \frac{1}{4}(-)^M T_{-K}^M + \frac{1}{4}T_K^{-M} + \frac{1}{4}(-)^M T_{-K}^{-M}$
$\boldsymbol{T}(a)\boldsymbol{C}_n, U', \sigma_{\mathrm{v}}$	M even: $\cos nM\varphi\cos 2\pi Kz/a$
	M odd: $\cos nM\varphi\sin 2\pi Kz/a$
10 $\boldsymbol{T}_c(a/2)\boldsymbol{S}_{2n}$	$\frac{1}{4}T_K^M + \frac{1}{4}(-)^K T_K^{-M} + \frac{1}{4}(-)^M T_{-K}^{-M} + \frac{1}{4}(-)^{M+K} T_{-K}^M$
$\boldsymbol{T}(a)\boldsymbol{C}_n, (\sigma_{\mathrm{v}}\vert\frac{1}{2}), U'$	K, M even: $\cos nM\varphi\cos 2\pi Kz/a$
	K even, M odd: $\cos nM\varphi\sin 2\pi Kz/a$
	K odd, M even: $\sin nM\varphi\sin 2\pi Kz/a$
	K, M odd: $\sin nM\varphi\cos 2\pi Kz/a$
11 $\boldsymbol{T}(a)\boldsymbol{D}_{nh}$	$\frac{1}{4}T_K^M + \frac{1}{4}T_{-K}^M + \frac{1}{4}T_K^{-M} + \frac{1}{4}T_{-K}^{-M}$
$\boldsymbol{T}(a)\boldsymbol{C}_n, U, \sigma_{\mathrm{v}}$	$\cos nM\varphi\cos 2\pi Kz/a$
12 $\boldsymbol{T}_c(a/2)\boldsymbol{C}_{nh}$	$\frac{1}{4}T_K^M + \frac{1}{4}(-)^K T_K^{-M} + \frac{1}{4}T_{-K}^{-M} + \frac{1}{4}(-)^K T_{-K}^M$
$\boldsymbol{T}(a)\boldsymbol{C}_n, (\sigma_{\mathrm{v}}\vert\frac{1}{2}), \sigma_{\mathrm{h}}$	K even: $\cos 2\pi Kz/a\cos nM\varphi$
	K odd: $\sin 2\pi Kz/a\sin nM\varphi$
13 $\boldsymbol{T}^1_{2n}(a/2)\boldsymbol{D}_{nh}$	$\frac{1}{4}Z_K^M + \frac{1}{4}Z_{K-M}^{-M} + \frac{1}{4}Z_{M-K}^M + \frac{1}{4}Z_{-K}^{-M}$
$\boldsymbol{T}^1_{2n}(a/2)\boldsymbol{C}_n, U, \sigma_{\mathrm{v}}$	$\cos nM\varphi\cos 2\pi(2K-M)z/a$

structure whose left and right conformations have isomorphic but different symmetry groups). Finally, taking into account that some of the products $\boldsymbol{ZP}$ result in the same group, we get altogether 13 infinite families of the line groups (table 1). It should be noted that $\boldsymbol{C}_n$ and $\boldsymbol{D}_n$

are compatible with any screw axis, even without translational periodicity. Hence, any chiral quasi-1D crystal has symmetry described by a line group of either first or fifth family, and here pertain all the *incommensurate* (without translational periodicity) structures.

Next important structural characteristic of a line group is that all roto-helical transformations form an invariant subgroup $\boldsymbol{L}^{(1)}$, which is the maximal subgroup belonging to the first family line groups $\boldsymbol{T}_Q(f)\boldsymbol{C}_n$: for 2–8 families it is a halving subgroup, while for 9–13 families it is an index four subgroup.

The existence of the $\boldsymbol{C}_n$ subgroup in the point factor reflects uniqueness of the screw-axis (for $n > 1$). Indeed, the same $\boldsymbol{L}^{(1)}$ is obtained as $\boldsymbol{T}_{Q'_s}(f)\boldsymbol{C}_n$ for $Q'_s = Q'n/(Q's+n)$ (giving the helical generator $(C_{Q'}C_n^s|f)$) for s integer. *To this end* we use convention that Q is the greatest finite among Q'_s, being

$$Q = \begin{cases} Q' & \text{if } n \leqslant Q' \\ \dfrac{nQ'}{n + Q' + Q'\left[-\frac{n}{Q'}\right]} & \text{if } n \geqslant Q', \end{cases} \tag{3}$$

($[x]$ and $\{x\}$ are integral and fractional parts of x). For commensurate cases, $q' = q'/r'$ we get (LCM denotes the least common multiple)

$$Q = \frac{q}{r}, \qquad \text{with} \quad q = \mathrm{LCM}(q', n) = n\tilde{q}, \quad r = \frac{q}{n}\left\{\frac{r'n}{q'}\right\}. \tag{4}$$

For translational group we get $\boldsymbol{T}(a)\boldsymbol{C}_n = \boldsymbol{T}^1_n(a)\boldsymbol{C}_n$ (i.e. finite greatest $Q = q = n$ is for $r = 1$; $\tilde{q} = 1$), while in zig-zag cases $\boldsymbol{T}^1_2(a/2)\boldsymbol{C}_n = \boldsymbol{T}^1_{2n}(a/2)\boldsymbol{C}_n$ (i.e. $Q = 2n$, $r = 1$, $\tilde{q} = 2$). Generally, with this convention the translational period of the commensurate line group is $a = f\tilde{q}$, while the order of the principle axis of the isogonal group is q. To unify notation, for the incommensurate helical factors of the line groups of families 1 and 5, we also write $\boldsymbol{T}^r_q(f)$, assuming $q = Q$ irrational and $r = 1$.

Very practical in some of the forthcoming considerations are screw-axis dependent *helical coordinates*, $(\rho, \tilde{\varphi}, \tilde{z})$, related to the cylindrical ones (ρ, φ, z) by

$$\rho = \rho, \qquad z = \frac{h}{\sqrt{4\pi^2\rho^2 + h^2}}\tilde{z}, \qquad \varphi = \tilde{\varphi} + \frac{2\pi}{\sqrt{4\pi^2\rho^2 + h^2}}\tilde{z}. \tag{5}$$

For fixed ρ and $\tilde{\varphi}$, coordinate curve $(\rho, \tilde{\varphi}, \tilde{z})$ is a helix with step $h = Qf$ (for commensurate groups this gives $h = na/r$, and particularly in the achiral cases $h = na$) on the cylinder of radius ρ coaxial to the z-axis. Such helices are invariant under the helical groups: any point of a helix is mapped into the same helix by any of the helical transformation.

The action (1) of the line group transformation ℓ on the function over Euclidean space $\mathbb{R}^3$ leaves the radial (cylindrical) coordinate ρ invariant, i.e. it is reduced to the space $\mathcal{L}(S^1 \times \mathbb{R})$ of the functions $F(\varphi, z)$ over cylinder. Further, the action of any line group transformation can be derived by combining the action of the following generators (in the cylindrical and helical coordinates, respectively):

$$\left(C^r_q\middle|f\right)(\varphi, z) = \left(\varphi + \frac{2\pi r}{q}, z + f\right), \qquad \left(C^r_q\middle|f\right)(\tilde{\varphi}, \tilde{z}) = \left(\tilde{\varphi}, \tilde{z} + \frac{r}{q}\sqrt{4\pi^2\rho^2 + h^2}\right),$$

$$C_n(\varphi, z) = \left(\varphi + \frac{2\pi}{n}, z\right), \qquad C_n(\rho, \tilde{\varphi}, \tilde{z}) = \left(\tilde{\varphi} + \frac{2\pi}{n}, \tilde{z}\right),$$

$$(I|f)(\varphi, z) = (\varphi, z + f), \qquad (I|f)(\tilde{\varphi}, \tilde{z}) = \left(\tilde{\varphi} - \frac{2\pi}{h}f, \tilde{z} + \frac{\sqrt{4\pi^2\rho^2 + h^2}}{h}f\right),$$

$$
\begin{aligned}
&U(\varphi, z) = (-\varphi, -z), && U(\tilde{\varphi}, \tilde{z}) = (-\tilde{\varphi}, -\tilde{z}),\\
&C_n\sigma_{\mathrm{h}}(\varphi, z) = \left(\varphi + \frac{2\pi}{n}, -z\right), && C_n\sigma_{\mathrm{h}}(\tilde{\varphi}, \tilde{z}) = \left(\tilde{\varphi} + 2\frac{2\pi}{\sqrt{4\pi^2\rho^2 + h^2}}\tilde{z}, -\tilde{z}\right),\\
&C_n\sigma_{\mathrm{v}}(\varphi, z) = \left(-\varphi + \frac{2\pi}{n}, z\right), && C_n\sigma_{\mathrm{v}}(\tilde{\varphi}, \tilde{z}) = \left(-\tilde{\varphi} - 2\frac{2\pi}{\sqrt{4\pi^2\rho^2 + h^2}}\tilde{z} + \frac{2\pi}{n}, \tilde{z}\right).
\end{aligned}
\tag{6}
$$

Note that, for $n = 0$ the last two equations give laws of transformation under the mirror planes. Also note that in the helical coordinates C_n and $\left(C_q^r \middle| f\right)$ change just a single coordinate: $\tilde{\varphi}$ and $\tilde{z}$, respectively.

3. Invariant functions

We look for the subspace of the invariant functions $H(\varphi, z)$ (or $\tilde{H}(\tilde{\varphi}, \tilde{z})$) in the space $\mathcal{L}(S^1 \times \mathbb{R})$. The condition of invariance (2) becomes

$$
\ell H(\varphi, z) = H(\varphi, z), \qquad \ell \tilde{H}(\tilde{\varphi}, \tilde{z}) = \tilde{H}(\tilde{\varphi}, \tilde{z}). \tag{7}
$$

Each line group element imposes one condition, but the independent set of equations (2) is given by the action of the generators only. Using the generators (given in table 1) and the corresponding action from (6), two or more equations (for each line group) are found and simultaneously solved.

The subspace of invariant functions will be given by its basis, the elements of which are called *harmonics* (of the line groups). At first, we will find harmonics of the first family, and then, by analysing the action of the remaining generators to the first family harmonics, the bases for all the other families will be derived.

3.1. Harmonics of the first family

As the first family line groups are Abelian, their generators have common eigenbasis in this space:

$$
F_\omega^M(\varphi, z) \stackrel{\mathrm{def}}{=} \mathrm{e}^{\mathrm{i}M\varphi}\,\mathrm{e}^{\mathrm{i}2\pi\omega z}, \qquad M = 0, \pm 1, \ldots, \quad \omega \in \mathbb{R}, \tag{8}
$$

which is orthogonal: $\int_0^{2\pi}\int_{-\infty}^{\infty} F_\omega^{M^*}(\varphi, z) F_{\omega'}^{M'}(\varphi, z)\,\mathrm{d}\varphi\,\mathrm{d}z = 2\pi\delta_{MM'}\delta(\omega - \omega')$ (where $\delta_{MM'}$ and $\delta(\omega - \omega')$ are Kronecker delta and Dirac's delta function, respectively). The eigenvalues of the generators C_n and $\left(C_q^r \middle| f\right)$ corresponding to these functions, $\exp(-\mathrm{i}2\pi M/n)$ and $\exp(-\mathrm{i}2\pi(Mr/q + \omega f))$ define the subspaces of irreducible representations.

The first two equation of (6) and condition (2) in the case of functions (8), select harmonics H_ω^M as the eigenfuctions for the eigenvalue one, i.e.:

$$
C_n H_\omega^M(\varphi, z) = H_\omega^M(\varphi, z), \qquad M = n\tilde{M}, \quad \tilde{M} = 0, \pm 1, \ldots, \tag{9}
$$

$$
\left(C_q^r \middle| f\right) H_\omega^M(\varphi, z) = H_\omega^M(\varphi, z), \qquad Mr + \omega f q = 0, \pm q, \pm 2q, \ldots, \tag{10}
$$

Combining these two conditions, one gets $\tilde{M}nr + \omega f = 0, \pm q, \pm 2q, \ldots$. The integers on the left are provided only by the special values $\omega = (-\tilde{M}nr/q + K)/f$ $(K = 0, \pm 1, \ldots)$. Therefore, the first family line group harmonics are

$$
S_K^M(\varphi, z) \stackrel{\mathrm{def}}{=} F^{nM}_{(-Mnr/q+K)/f}(\varphi, z), \qquad M, K = 0, \pm 1, \ldots \tag{11}
$$

with orthogonality relations

$$
\int_0^{\frac{2\pi}{n}}\int_0^f S_K^{M^*}(\varphi, z) S_{K'}^{M'}(\varphi, z)\,\mathrm{d}\varphi\,\mathrm{d}z = \frac{2\pi f}{n}\delta_{MM'}\delta_{KK'}. \tag{12}
$$

Repeating the same procedure for the basis $F^M_\omega(\tilde\varphi,\tilde z)$, or directly substituting cylindrical coordinates in (11), we find these functions in the helical coordinates:

$$S^M_K(\tilde\varphi,\tilde z)=F^{nM}_{Kq/r\sqrt{4\pi^2\rho^2+h^2}}(\tilde\varphi,\tilde z)=\mathrm{e}^{\mathrm{i}nM\tilde\varphi}\,\mathrm{e}^{\mathrm{i}\frac{2\pi Kq}{r\sqrt{4\pi^2\rho^2+h^2}}\tilde z},\qquad M,K=0,\pm1,\ldots, \tag{13}$$

where M and K count rotational and helical harmonics over $\tilde\varphi$ and $\tilde z$, respectively.

For the commensurate groups, when q is an integer and $a=\tilde q f$ the harmonics become

$$S^M_K(\varphi,z)=F^{nM}_{(-Mr+K\tilde q)/a}(\varphi,z),\qquad M,K=0,\pm1,\ldots. \tag{14a}$$

In the special cases, when the screw-axis degenerates to pure translations $\boldsymbol{T}^0_1(a)$ (coordinate helices $\tilde z$ are vertical lines, and condition (10) is M-independent) and $\boldsymbol{T}^1_{2n}(a)$ one gets, respectively

$$T^M_K(\varphi,z)=F^{nM}_{K/a}(\varphi,z),\qquad M,K=0,\pm1,\ldots, \tag{14b}$$

$$Z^M_K(\varphi,z)=F^{nM}_{(-M+2K)/a}(\varphi,z),\qquad M,K=0,\pm1,\ldots. \tag{14c}$$

3.2. The other families

Families 2–13 have elements that do not commute with the roto-helical transformations. Therefore, the invariants of these groups form a nontrivial subspace of the first family harmonics space. Moreover, eigenbasis of $\boldsymbol{L}^{(1)}$ cannot be the basis of this subspace and the harmonics of 2–13 families are linear combinations of harmonics (11). It is sufficient to find action of the coset representatives (given in table 1) onto the roto-helical harmonics. It turns out that this action always has the following form $gS^M_K=\alpha S^{M'}_{K'}$

$$\begin{aligned}
&C_{2n}\sigma_{\mathrm h}S^M_K(\varphi,z)=\mathrm{e}^{-\mathrm{i}\pi M}S^M_{-K+2\frac{nMr}{q}}(\varphi,z),\\
&(\sigma_{\mathrm v}|a/2)S^M_K(\varphi,z)=\mathrm{e}^{\mathrm{i}2\pi\frac{nMr}{q}}S^{-M}_{K-2\frac{nMr}{q}}(\varphi,z),\\
&UF^M_K(\varphi,z)=S^{-M}_{-K}(\varphi,z),\\
&\sigma_{\mathrm h}S^M_K(\varphi,z)=S^M_{-K+2\frac{nMr}{q}}(\varphi,z),\\
&\sigma_{\mathrm v}S^M_K(\varphi,z)=S^{-M}_{K-2\frac{nMr}{q}}(\varphi,z).
\end{aligned} \tag{15}$$

While the U-axis can be combined with any helical axis, the rest of the generators are compatible only with the achiral roto-helical subgroups (thus, only harmonics (14*b*) and (14*c*) are to be considered). Further, as the square of an additional generator g is always from the roto-helical subgroup $\boldsymbol{L}^{(1)}$, the harmonic invariant under g (and therefore under the group $\boldsymbol{L}^{(1)}+g\boldsymbol{L}^{(1)}$) is of the form $S^M_K+gS^M_K$. This way we directly find the harmonics of families 2–8, while the procedure is to be repeated, acting on these newharmonics by the remaining coset representatives for families 9–13. All the line group harmonics are listed in table 1. To get the normalization $\int_0^{\frac{2\pi}{n}}\int_0^f H^{M*}_K(\varphi,z)H^{M'}_{K'}(\varphi,z)\,\mathrm{d}\varphi\,\mathrm{d}z=\delta_{MM'}\delta_{KK'}$, the tabulated harmonics should be divided by the factors $\sqrt{\frac{2\pi f}{n}}$, $\sqrt{\frac{\pi f}{n}}$ and $\sqrt{\frac{\pi f}{2n}}$ for families 1, 2–8 and 9–13, respectively. The exceptions are normalization factors:

(i) $\sqrt{\frac{2\pi f}{n}}$ of: H^M_0 for families 2 and 3, $H^M_{M/2}$ for family 4, H^0_0 for families 5 and 9–13, and H^0_K for families 6–8;

(ii) $\sqrt{\frac{\pi f}{n}}$ of: $H^{M\neq0}_0$ and $H^0_{K\neq0}$ for families 9–12, and $H^{M\neq0}_{M/2}$ for family 13.

The harmonics with $M = 0$ are φ-independent (and also $\tilde{\varphi}$-independent) functions, i.e. they are constants on the circles around the z-axis. However, harmonics with $K = 0$ are constant along the coordinate helices $\tilde{z}$, and only when $\boldsymbol{L}^{(1)} = \boldsymbol{T}(a)$ (families 2, 3, 6, 7, 9–12) they are constant along the z-axis. For $M \neq 0$, harmonic H_K^M is invariant under $\boldsymbol{C}_{nM}$, as its rotational period is $2\pi/n|M|$: $H_K^M(\varphi + 2\pi/n|M|, z) = H_K^M(\varphi, z)$; only for $M = 1$ rotational period $2\pi/n$ of the harmonics coincides with the rotational symmetry of the system. Thus, rotational symmetry of harmonic is larger than that of the system, except for $M = \pm 1$ when they coincide. The analogue is true for K and the periodicity in $\tilde{z}$ (or z). In other words, line group $\boldsymbol{L}$ is a subgroup of the symmetry group of its harmonics H_K^M, comprising the full symmetry only of the harmonics with $|M| = |K| = 1$.

3.3. Invariants in the whole space

After the basis of harmonics in the space of the functions over cylinder is found, we can easily complete it to the basis of invariants in $\mathcal{L}(\mathbb{R}^3)$:

$$U_{KI}^M(\boldsymbol{r}) = R_{IMK}(\rho) H_K^M(\varphi, z). \tag{16}$$

Here, for any fixed M and K the functions $R_{IMK}(\rho)$ form a basis in the space of functions over ρ. The singularity at $\rho = 0$ of the cylindrical and helical coordinates (any function $F(\rho, \varphi, z)$ at $\rho = 0$ must be φ-independent) implies that for $M \neq 0$ the functions $R_{IMK}(\rho)$ vanish at $\rho = 0$, as combined with φ-dependent harmonics.

For various applications it is advantageous to use the basis

$$U_{Kb}^M(\boldsymbol{r}) = \sqrt{b} J_{|nM|}(b\rho) H_K^M(\varphi, z), \qquad b \in \mathbb{R} \tag{17}$$

(with Bessel functions $J_{|nM|}(b\rho)$ normalized as $\int_0^\infty J_{|nM|}(b\rho) J_{|nM|}(b'\rho)\rho \, \mathrm{d}\rho = \frac{1}{b}\delta(b - b')$), as this is the eigenbasis of kinetic energy:

$$\Delta U_{Kb}^M(\boldsymbol{r}) = -\left(b^2 + \left(2\pi \frac{K\tilde{q} - Mr}{a}\right)^2\right) U_{Kb}^M(\boldsymbol{r}). \tag{18}$$

4. Covariants and Bloch functions

Bloch theorem states that the (quasi)particle eigenfunctions of the system translationally periodic along the z-axis are of the form $\Psi_k(\boldsymbol{r}) = \mathrm{e}^{\mathrm{i}kz} u(\boldsymbol{r})$, where $u(\boldsymbol{r})$ is invariant (i.e. periodic) function: $u(\rho, \varphi, z + ta) = u(\rho, \varphi, z)$. Obviously, the first factor defines the rule of the transformation under translations, $\Psi_k(\rho, \varphi, z + ta) = \mathrm{e}^{\mathrm{i}kat} \Psi_k(\rho, \varphi, z)$, singling out the irreducible representation $D^{(k)}(ta) = \mathrm{e}^{\mathrm{i}kat}$ of the translational group, while only the second factor specifies the function obeying this transformation rule.

To generalize this concept to full line group symmetry, we note that the translation group is Abelian, having only one-dimensional irreducible representations and that this property is shared first family line groups exclusively, while all the other families have two- and/or four-dimensional irreducible representations as well. Therefore, the functions are grouped into the *multiplets* of covariants $\Psi^{(\lambda)l}(\boldsymbol{r})$ ($l = 1, \ldots, |\lambda|$) corresponding to the irreducible representations $D^{(\lambda)}$ of the dimension $|\lambda|$ ($|\lambda| = 1, 2, 4$), which for each $\ell \in \boldsymbol{L}$ satisfy

$$\ell \Psi^{(\lambda)l}(\boldsymbol{r}) \stackrel{\text{def}}{=} \Psi^{(\lambda)l}(\ell^{-1}\boldsymbol{r}) = \sum_{l'=1}^{|\lambda|} D_{l'l}^{(\lambda)}(\ell) \Psi^{(\lambda)l'}(\boldsymbol{r}). \tag{19}$$

Consequently, taking all irreducible representations λ, it is possible to find *symmetry adapted basis* $\Psi_C^{(\lambda)l}(\boldsymbol{r})$ in the space of functions over $\boldsymbol{r}$. The basis functions transformation rule is given

by (19) where $C = 1, 2, \ldots$ counts linearly independent covariant functions (or *multiplets*) which transforms by the same rule.

To describe such a basis, we again firstly consider SAB in the space of the functions over cylinder, denoting the functions satisfying the same transformations rules (19) as $\Phi^{(\lambda)l}(\varphi, z)$. Obviously, simultaneously multiplying the whole multiplet $\Phi^{(\lambda)l}(\varphi, z)$ by the same invariant function $H(\varphi, z)$, we obtain functions $\Phi^{(\lambda)l}(\varphi, z)H(\varphi, z)$ satisfying the same transformation rules (19). Therefore, having one representative multiple $\Phi_{00}^{(\tilde{\lambda})l}(\varphi, z)$ for each irreducible representation, SAB is obtained by multiplying it by the whole basis of the harmonics (thus, C is a pair of the indices K and M of the invariants):

$$\Phi_{KM}^{(\lambda)l}(\varphi, z) = \Phi_{00}^{(\lambda)l}(\varphi, z)H_K^M(\varphi, z). \tag{20}$$

(The invariant functions transform according to the identical representation, $D^{(\lambda)}(\ell) = 1$, i.e. $\Phi_{00}^{(\lambda)l}(\varphi, z) = 1$ and the corresponding harmonics make a part of the SAB.)

It is now straightforward to see the generalization of the Bloch theorem to the line group symmetry. Namely,

$$\Psi^{(\lambda)l}(\boldsymbol{r}) = \Phi_{00}^{(\lambda)l}(\varphi, z)u(\boldsymbol{r}), \tag{21}$$

and by combining it with (16), we get SAB in the whole space $\mathcal{L}(\mathbb{R}^3)$:

$$\Psi_{IKM}^{(\lambda)l}(\boldsymbol{r}) = \Phi_{00}^{(\lambda)l}(\varphi, z)R_{IMK}(\rho)H_K^M(\varphi, z). \tag{22}$$

The result obtained enables expansion of any function $\Psi^{(\lambda)l}(\boldsymbol{r})$ over SAB:

$$\Psi^{(\lambda)l}(\boldsymbol{r}) = \sum_{IKM} \alpha_{IKM}\Phi_{00}^{(\lambda)l}(\varphi, z)R_{IMK}(\rho)H_K^M(\varphi, z); \tag{23}$$

where the sum runs over all allowed values of I, M and K, while the amplitudes are scalar products: $\alpha_{IKM} = \left(\Psi_{IKM}^{(\lambda)l}, \Psi^{(\lambda)l}\right) = \int \Psi_{IKM}^{(\lambda)l^*}(\rho, \varphi, z)\Psi^{(\lambda)l}(\rho, \varphi, z)\rho\,\mathrm{d}\rho\,\mathrm{d}\varphi\,\mathrm{d}z$. We also introduce expansions over harmonics with the radial functions being independent of the choice of $R_{IMK}(\rho)$:

$$\begin{aligned}
&\Psi^{(\lambda)l}(\boldsymbol{r}) = \sum_{KM} \alpha_K^M(\rho)\Phi_{00}^{(\lambda)l}(\varphi, z)H_K^M(\varphi, z),\\
&\alpha_K^M(\rho) = \sum_I \alpha_{IKM}R_{IMK}(\rho) = \rho\int_0^{2\pi}\int_{-\infty}^{\infty} \Phi_{KM}^{(\lambda)l^*}(\varphi, z)\Psi^{(\lambda)l}(\rho, \varphi, z)\,\mathrm{d}\varphi\,\mathrm{d}z.
\end{aligned} \tag{24}$$

Knowing harmonics (table 1), it remains to find the representative functions $\Phi_{00}^{(\lambda)l}(\varphi, z)$ for each irreducible representation of the line groups. However, as the number of different irreducible representations of the 13 families of line groups is very large this exhaustive task is beyond the scope of this paper. But we will sketch the general solution for the first family, and give the result in a comprehensive form for families 5 and 13, which are important for the applications to carbon nanotubes (section 5).

For the first family, the irreducible representations are classified [7, 10] by the pairs $(\tilde{k}, \tilde{m})$ of helical and angular quasi-momenta:

$${}_{\tilde{k}}A_{\tilde{m}}\left(\left(C_q^r\middle|f\right)^t C_n^s\right) = \mathrm{e}^{\mathrm{i}\tilde{k}ft}\,\mathrm{e}^{\mathrm{i}\tilde{m}\frac{2\pi}{n}s}, \qquad \tilde{k} \in \left(-\frac{\pi}{f}, \frac{\pi}{f}\right], \qquad \tilde{m} \in \left(-\frac{n}{2}, \frac{n}{2}\right]. \tag{25}$$

As the basis (8) satisfies $\left(C_q^r\middle|f\right)F_\omega^M(\varphi, z) = \mathrm{e}^{-\mathrm{i}2\pi(Mr/q+\omega f)}F_\omega^M(\varphi, z)$ and $C_nF_\omega^M(\varphi, z) = \mathrm{e}^{-\mathrm{i}2\pi M/n}F_\omega^M(\varphi, z)$, the representative functions $\Phi_{00}^{(\tilde{k}\tilde{m})}(\varphi, z)$ and SAB are

$$\Phi_{00}^{(\tilde{k}\tilde{m})}(\varphi, z) = F_{-\tilde{k}h/\sqrt{4\pi^2\rho^2+h^2}}^{-\tilde{m}}(\tilde{\varphi}, \tilde{z}), \qquad \Phi_{KM}^{(\tilde{k}\tilde{m})}(\varphi, z) = S_{-\tilde{k}f/2\pi+K}^{-\tilde{m}+nM}(\varphi, z). \tag{26}$$

For the other line group families, parities do not commute with roto-helical symmetries, which results two- or four-dimensional irreducible representations [7, 10]. One-dimensional

ones appear for some particular values of helical and angular quasi-momenta, while pairs or quadruples of the pairs $(\tilde{k}, \tilde{m})$ are combined in two- and four-dimensional representations. A choice of a particular pair $(\tilde{k}, \tilde{m})$ determines both λ and l. For an additional generator g (like U, $\sigma_{\rm v}$ and $\sigma_{\rm v}$) we define g-parity Π^g of a representation λ as $\Pi^g = 1$ if $D^{(\lambda)}(g) = I$ (identity matrix), $\Pi^g = -1$ if $D^{(\lambda)}(g) = -I$ and $\Pi^g = 0$ otherwise. This way, SAB is defined by the quasi-momenta quantum numbers and parities. For the fifth family the only parity is Π^U, and for the 13th family parities are Π^U, $\Pi^{\rm v}$ and $\Pi^{\rm h}$ (corresponding to the generators U, $\sigma_{\rm v}$ and $\sigma_{\rm v}$). Introducing notation $\tilde{\Pi}^g$ being equal to -1 if $\Pi^g = -1$ while $\tilde{\Pi}^g = 1$ otherwise, the representative functions of the fifth and 13th family are respectively given by

$$\Phi_{00}^{\tilde{k}\tilde{m}\Pi^U}(\varphi, z) = \exp\left(-\mathrm{i}\tilde{\Pi}^U\left(\tilde{m}\varphi + \left(\tilde{k} - \frac{2\pi\tilde{m}r}{f}\right)z\right)\right), \tag{27}$$

$$\Phi_{00}^{\tilde{k}\tilde{m}\Pi^U\Pi^h\Pi^v}(\varphi, z) = \exp\left(-\mathrm{i}\tilde{\Pi}^U\left(\tilde{\Pi}^{\rm v}\tilde{m}\varphi + \tilde{\Pi}^{\rm h}\left(\tilde{k} - \frac{2\pi\tilde{m}r}{f}\right)z\right)\right). \tag{28}$$

The identical representation of all the families is obtained for $\tilde{k} = \tilde{m} = 0$, and $\Pi^g = 1$ for all the involved parities. This gives a unit representative function for the invariants. Note that when an invariant is a real function, the amplitudes satisfy $\alpha_K^M(\rho) = \alpha_{-K}^{-M}(\rho)$. Consequently, in this case for families 5 and 9–13 the amplitudes are real, while $\alpha_K^M(\rho) = \alpha_K^{-M}(\rho)$ for families 2–4, and $\alpha_K^M(\rho) = \alpha_{-K}^M(\rho)$ for families 6–8.

5. Applications to carbon nanotubes

To illustrate possible applications of the developed concepts, we consider single-wall carbon nanotubes (SWCNT) [1] which have huge symmetry, described by commensurate line groups [11, 12] and which are the most studied and the most promising nano-systems. The symmetry group $\boldsymbol{L}$ of SWCNT (n_1, n_2) is from the fifth family when $n_1 > n_2 > 0$ (chiral tubes) or from 13th family when $n_1 > n_2 = 0$ (zig-zag) or $n_1 = n_2 > 0$ (armchair tubes), with the parameters defined [11] in terms of n_1 and n_2:

$$n = \mathrm{GCD}(n_1, n_2), \qquad q = 2\left(n_1^2 + n_1 n_2 + n_2^2\right)\big/ n\mathcal{R}, \qquad a = \sqrt{3}\frac{D\pi}{n\mathcal{R}}. \tag{29}$$

Here $a_0 = 2.461$ Å is a graphene lattice period, $D = \frac{n}{\pi}\sqrt{\frac{\tilde{q}\mathcal{R}}{2}}a_0$ is the tube diameter, $\mathcal{R} = \mathrm{GCD}(2n_1 + n_2, n_1 + 2n_2)/n$, while r is a more complicated number theoretical function [11].

SWCNT is a single-orbit systems, i.e. taking an arbitrary atom (denoted as C_{000}), each other atom C_{tsu} is obtained by a symmetry transformation $\ell_{tsu} = \left(C_q^r \middle| a\middle/\tilde{q}\right)^t C_n^s U^u$ (for $t = 0, \pm 1, \ldots, n = 0, \ldots, n-1, u = 0, 1$). These transformations form the fifth family subgroup $\boldsymbol{L}^{(5)}$ of $\boldsymbol{L}$, being the full symmetry group for the chiral tubes, and its halving subgroup for achiral ones. In order to incorporate the convention that the x-axis coincides with the U-axis of the symmetry group, the reference atom C_{000} is positioned as

$$\rho_{000} = D/2, \qquad \varphi_{000} = 2\pi\frac{n_1 + n_2}{nq\mathcal{R}}, \qquad z_{000} = \frac{n_1 - n_2}{\sqrt{6}nq\mathcal{R}}a_0. \tag{30}$$

5.1. Potentials

The fields produced by nanotubes are necessarily invariant functions. Indeed, for any pairwise interaction $v(\boldsymbol{r}, \boldsymbol{r}_{tsu})$ of a probe particle (positioned at $\boldsymbol{r}$) with the nanotube atom C_{tsu} (positioned at $\boldsymbol{r}_{tsu}$), the total potential is $V(\boldsymbol{r}) = \sum_{tsu} v(\boldsymbol{r}, \boldsymbol{r}_{tsu})$. When the symmetry

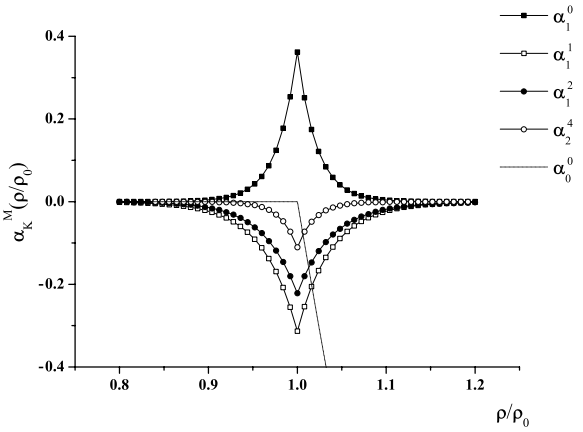

Figure 1. Potential of the carbon nanotube (13, 13) ($\boldsymbol{L} = \boldsymbol{T}_{26}^{1}(1.23\ \text{Å})\boldsymbol{D}_{13\text{h}}$, $\rho_0 = D/2 = 8.82$ Å) induced by the Coulomb atomic potential. Non-negligible expansion coefficients $\alpha_K^M(\rho)$ plotted in the significant range $0.75D/2 < \rho < 1.2D/2$.

transformation ℓ is applied, the potential $\ell V(\boldsymbol{r}) = \sum_i V(\boldsymbol{r}, \ell^{-1}\boldsymbol{r}_{tsu})$ is invariant, as only its terms are permuted. Therefore, its general form is given by (24). Further, the terms with $|K| = |M| = 1$ cannot vanish, as in that case the system would have apparently larger symmetry than $\boldsymbol{L}$.

At first we analytically discuss the ionic *Coulomb* potential, yielding the potential of the whole nanotube $V(\boldsymbol{r}) = \sum_{tsu} \frac{1}{|\boldsymbol{r}-\boldsymbol{r}_{tsu}|}$. The *Poisson equation* becomes $\Delta V(\boldsymbol{r}) = -4\pi \sum_{tsu} \delta(\boldsymbol{r} - \boldsymbol{r}_{tsu})$, and straightforward calculation gives the expansion over basis (17):

$$V(\boldsymbol{r}) = \sum_{K\,M} \int_0^\infty \alpha_K^{Mb} U_{Kb}^M(b\rho, \varphi, z)\,\mathrm{d}b, \qquad \alpha_K^{Mb} = \frac{8\pi}{D} \frac{U_{Kb}^{M*}\left(\frac{D}{2}, \varphi_{000}, z_{000}\right)}{b^2 + \left(2\pi \frac{2K-M}{a}\right)^2}. \tag{31}$$

The expansion amplitudes $\alpha_K^M(\rho)$ over normalzed harmonics H_K^M can easily be found in terms of modified Bessel functions $K_m(x)$ and $I_m(x)$. For example, for the achiral tubes (13th line group family, see figure 1), we get for $K = M = 0$, $K = M/2$ ($M \neq 0$ even) and otherwise, respectively

$$\alpha_0^0(\rho) = H_0^{0*}(\varphi_{000}, z_{000}) \begin{cases} 0, & \rho \leqslant \dfrac{D}{2}; \\ -4\pi \ln\left(\dfrac{\rho}{\frac{D}{2}}\right), & \rho > \dfrac{D}{2}, \end{cases}$$

$$\alpha_{\frac{M}{2}}^M(\rho) = \frac{2\pi}{nM} H_{\frac{M}{2}}^{M*}(\varphi_{000}, z_{000}) \begin{cases} \left(\dfrac{\rho}{\frac{D}{2}}\right)^{nM}, & \rho \leqslant \dfrac{D}{2}; \\ \left(\dfrac{\rho}{\frac{D}{2}}\right)^{-nM}, & \rho > \dfrac{D}{2}, \end{cases}$$

$$\alpha_K^M(\rho) = 4\pi\, H_K^{M*}(\varphi_{000}, z_{000}) \begin{cases} K_{nM}\left(2\pi \dfrac{|2K-M|}{a}\dfrac{D}{2}\right) I_{nM}\left(2\pi \dfrac{|2K-M|}{a}\rho\right), & \rho \leqslant \dfrac{D}{2}; \\ I_{nM}\left(2\pi \dfrac{|2K-M|}{a}\dfrac{D}{2}\right) K_{nM}\left(2\pi \dfrac{|2K-M|}{a}\rho\right), & \rho > \dfrac{D}{2}. \end{cases}$$

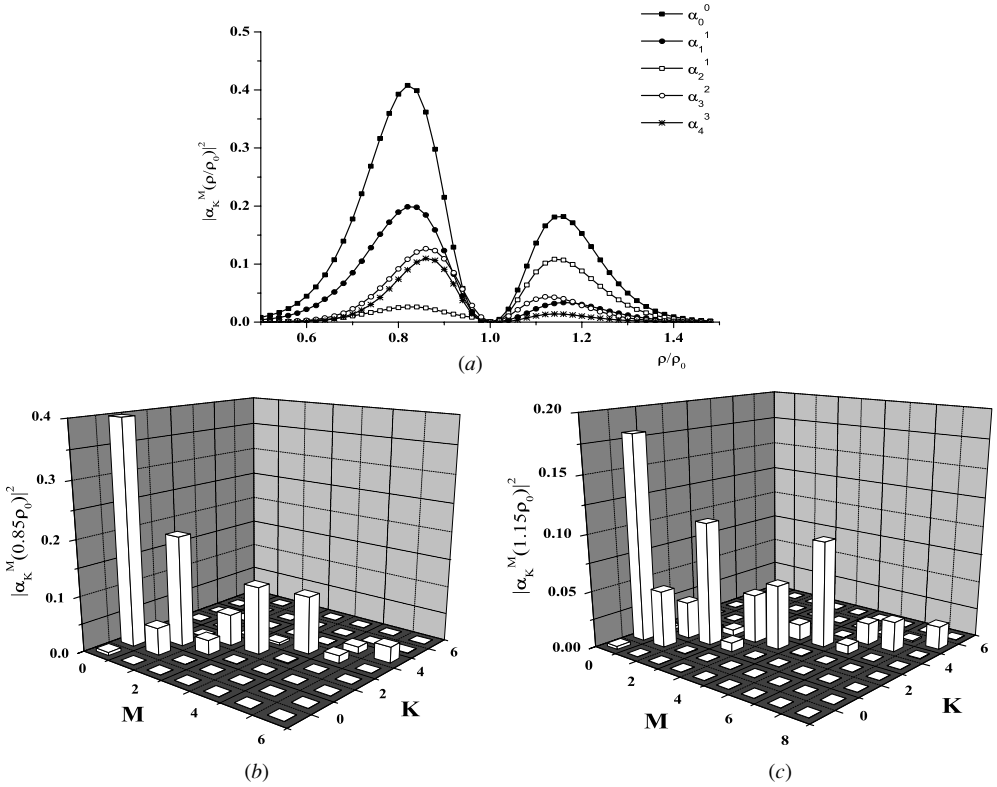

Figure 2. Bloch eigenstate of the carbon nanotube (4, 2) (with $\boldsymbol{L} = \boldsymbol{T}_{28}^{9}(0.8\ \text{Å})\boldsymbol{D}_2$ and radius $\rho_0 = D/2 = 2.07$ Å) corresponding to $\tilde{k} = \pi/10$ $f = 0.389\,993$ Å^{-1} and $\tilde{m} = 1$ (energy $E = -0.285$ eV). (a) Non-negligible expansion coefficients $\alpha_K^M(\rho)$ plotted in the significant range $0 < \rho < 1.5\rho_0$. ((b) and (c)) Harmonic expansion at particular radii $\rho = 0.85\rho_0$ and $\rho = 1.15\rho_0$. The greed of $50 \times 32 \times 32$ points over (ρ, φ, z) is used.

Another example has been discussed in the context of the layer–layer interaction of double-wall tubes [13]. Using Van der Waals pairwise potential, the total potential of a single wall tube has been numerically calculated and expanded over harmonics. The amplitudes $\alpha_K^M(\rho)$ rapidly decrease both with M and K, which has been used to show that the interaction between layers is very weak, even vanishing in some cases, making the double-wall tubes ideal component of nano-machines.

5.2. Bloch states and electronic density

For the chiral tubes ($n_1 > n_2 > 0$), the electronic bands for each $\tilde{k} \in (0, q\pi/na)$ (interior of the helical Brillouin zone) are double degenerate, and correspond to two-dimensional irreducible representations $E_{\tilde{k}}^{\tilde{m}}$ ($m = -q/2+1, \ldots, q/2$). In fact, the generator U reverses z-components of linear and angular momenta, making degenerate the Bloch states $\Psi^{(\tilde{k},\tilde{m})1} = \Psi^{(\tilde{k}\tilde{m})}(\boldsymbol{r})$ and $\Psi^{(\tilde{k},\tilde{m})2} = \Psi^{(-\tilde{k},-\tilde{m})}(\boldsymbol{r})$ (for both states $\Pi^U = 0$ and $\tilde{\Pi}^U = 1$). According to (27), the SAB (22) of the representation $E_{\tilde{k}}^{\tilde{m}}$ is

$$\Psi_{IKM}^{(\pm\tilde{k},\pm\tilde{m})1}(\boldsymbol{r}) = \exp\left(\mp \mathrm{i}\left(\tilde{m}\varphi + \left(\tilde{k} - \frac{2\pi\tilde{m}r}{f}\right)z\right)\right) R_{IMK}(\rho) H_K^M(\varphi, z), \tag{33}$$

where $H_K^M(\varphi, z)$ are the fifth family harmonics (table 1).

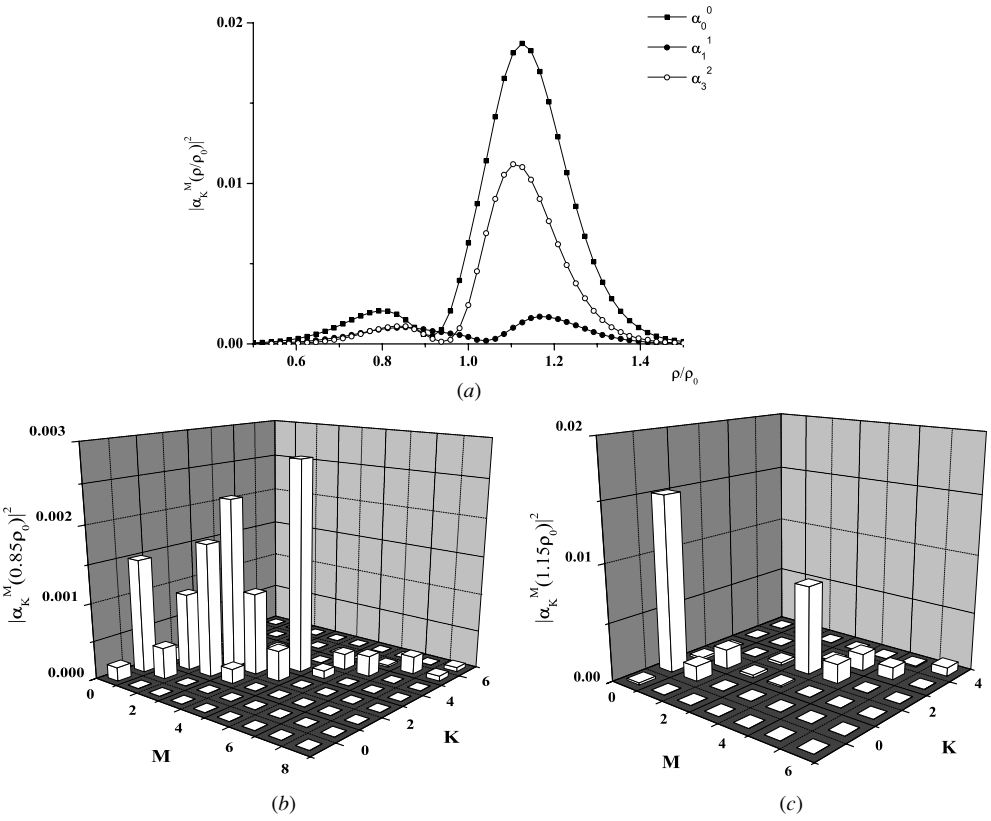

Figure 3. Electronic density of the carbon nanotube (4, 2). Panels (a)–(c) as in figure 2.

We are going to find the amplitudes $\alpha_K^M(\rho)$ in expansion (24) of the Hamiltonian eigenstates $\Psi^{(\tilde{k},\tilde{m})l}(\boldsymbol{r})$ over the found symmetry adapted basis. Within the tight-binding model, Bloch eigenfunctions are linear combination of N atomic orbitals (per atom) χ_i $(i = 1, \ldots, N)$: $\Psi^{(\tilde{k},\tilde{m})l}(\boldsymbol{r}) = \sum_{tsu,i} c_{tsu,i}^{(\tilde{k},\tilde{m})l} \chi_i\left(\ell_{tsu}^{-1}\boldsymbol{r}\right)$. Due to the symmetry the coefficients $c_{tsu,i}^{(\tilde{k},\tilde{m})l}$ are not independent; by abbreviating those associated with the reference atom, $c_i^{(\tilde{k},\tilde{m})l} = c_{000,i}^{(\tilde{k},\tilde{m})l}$, the eigenfunctions get inductive form [11]

$$\Psi^{(\tilde{k}\tilde{m})l}(\boldsymbol{r}) = \frac{1}{\sqrt{|\boldsymbol{L}^{(5)}|}} \sum_{tsu} \sum_{l'i} c_i^{(\tilde{k}\tilde{m})l'} D_{ll'}^{(\tilde{k}\tilde{m})*}(\ell_{tsu}) \ell_{tsu} \chi_i(\boldsymbol{r}). \tag{34}$$

This simplifies calculation of the amplitudes: when (34) is substituted in the scalar product $\alpha_{IMK} = \left(\Psi_{IKM}^{(\tilde{k}\tilde{m})l}(\boldsymbol{r}), \Psi^{(\tilde{k}\tilde{m})l}(\boldsymbol{r})\right)$, instead of the action on the atomic orbitals by the unitary operators ℓ_{tsu}, their inverses $\ell_{tsu}^{\dagger} = \ell_{tsu}^{-1}$ may be applied on the SAB functions on the left, giving by (19):

$$\alpha_{IMK} = \sum_{l'l''i} \left(\frac{1}{\sqrt{|\boldsymbol{L}^{(5)}|}} \sum_{tsu} D_{ll'}^{(\tilde{k}\tilde{m})*}(\ell_{tsu}) D_{ll''}^{(\tilde{k}\tilde{m})}(\ell_{tsu}) \right) c_i^{(\tilde{k}\tilde{m})l'} \left(\Psi_{IKM}^{(\tilde{k}\tilde{m})l''}(\boldsymbol{r}), \chi_i(\boldsymbol{r})\right).$$

After applying the orthogonality theorem [9] the braced factor reduces to $\delta_{l',l''}/|\lambda|$ (where $|\lambda|$ is the dimension of $D^{(\lambda)}$), and Bloch eigenstates are expressed through the amplitudes of the atomic orbitals:

$$\alpha_{IMK} = \frac{1}{2}\sum_{l'i} c_i^{(\tilde{k}\tilde{m})l'}\left(\Psi_{IKM}^{(\tilde{k}\tilde{m})l'}(\boldsymbol{r}), \chi_i(\boldsymbol{r})\right). \tag{35}$$

To get deeper insight into the last expansion, we use the simplest tight-binding model [14], with the single Slater-type orbital perpendicular to the nanotube cylinder:

$$\Phi(\boldsymbol{r}) = \sqrt{\frac{2Z_{\text{eff}}^7}{15\pi a_B^7}}|\boldsymbol{r} - \boldsymbol{r}_{000}|\left(\rho\cos\varphi - \frac{D}{2}\cos\varphi_0\right)\mathrm{e}^{-\frac{Z_{\text{eff}}}{a_{\text{B}}}|\boldsymbol{r}-\boldsymbol{r}_{000}|} \tag{36}$$

(a_{B} is the Bohr radius and $Z_{\text{eff}} \approx 3.81$).

For the tube (4, 2) we analyse the electronic state corresponding to the energy $E = -0.285$ eV. Its quantum numbers are $\tilde{k} = \frac{\pi}{10}, \tilde{m} = 1, U = 0$ (i.e. it transforms according to the irreducible representation ${}_{\tilde{k}=\frac{\pi}{10}}E_{\tilde{m}=1}$). Figure 2 shows the expansion of this state, performed numerically.

Finally, we calculate electronic density, being the sum $\varrho = \sum|\Psi^{(\tilde{k}\tilde{m})l}(\boldsymbol{r})|^2$ of the densities $|\Psi^{(\tilde{k}\tilde{m})l}(\boldsymbol{r})|^2$ of all the filled states, i.e. below the Fermi level. At zero temperature this is an invariant function, and can be expanded over the harmonics H_K^M. The results for the tube (4, 2) are presented in figure 3.

6. Conclusions

It has been shown that each covariant function (transforming according to an irreducible representation) of a line group may be factorized as a product of a representative function with the same transformation properties and an invariant function. The representative functions are determined only by symmetry, and may be found *a priori*, independently of the particular system (with given symmetry) or physical problem considered. This generalization of the Bloch theorem to the full line group symmetry, may be easily extended to some other type of systems, such as 3D crystals, for instance. Further, we found the bases of invariants, i.e. harmonics, for all the line groups. This enables us to compose the total symmetry adapted basis in the quantum-mechanical state space of any (commensurate or incommensurate) quasi-1D crystal (e.g. stereoregular polymers or nanotubes) from the representative functions and harmonics.

The results are used to expand the potentials and electronic density of carbon nanotubes over the harmonics, and electronic Bloch eigenstates over SAB. Transparently enough, significant amplitudes in these expansions correspond only to a few lowest harmonics ($K, M < 10$). This result is intuitively sound, having in mind that higher harmonics (for $K, M > 1$) have larger symmetry than the system itself.

This result can facilitate quantum-mechanical calculations of the properties of systems with line group symmetry. In fact, even in the most accurate numerical procedures, like density functional or Hartee–Fock codes, the choice of the basis functions in iterative procedures makes a compromise between the memory and run-time on the one side and accuracy on the other. Typically, a regular greed of hundreds of plane waves is used. However, the presented result inspires a new, symmetry-based scheme. Only a dozen of harmonics corresponding to the symmetry of a system are really significant. Even in the cases of the most complex quasi-one-dimensional systems, the number of such harmonics is less than 100. Moreover, the comparative accuracy is improved, as the contribution of the neglected part of the Hilbert space is *a priori* known to be negligible.

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