# Symmetry based properties of the transition metal dichalcogenide nanotubes

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**Abstract.** The full geometrical symmetry groups (the line groups) of the monolayered, 2Hb and 3R polytypes of the inorganic $MoS_2$ and $WS_2$ micro- and nanotubes of arbitrary chirality are found. This is used to find the coordinates of the representative atoms sufficient to determine completely the geometrical structure of the tubes. Then some physical properties which can be deduced from the symmetry are discussed: electron band degeneracies, selection rules, general forms of the second rank tensors and potentials, phonon spectra.

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## 1 Introduction

Layered structures of the transition metal dichalcogenides $MS_2$ (M = Mo,W) are unstable against folding [1] and this can lead to a formation of nanotubes [2] or microtubes [3]. The obtained tubes have high symmetry, which is relevant both for profound insight into their physical properties and for simplification of the calculations. The aim of this paper is to find the symmetry of ideal single-layered rhombohedral 3R and hexagonal 2Hb polytypes of $MS_2$ [1] folded into tubes, and to discuss their general symmetry properties.

In Section 2, after a brief reminder of the line groups, the symmetry groups for all the chiralities of the monolayered (*i.e.* consisting of only one sulfur–transition metal–sulfur molecular layer) 2Hb and 3R single-layered polytypes of the $MS_2$ nanotubes are determined. A convenient choice of the lattice vectors enables this task to be performed in analogy with single-wall carbon nanotubes [4]. It turns out that the obtained symmetry groups are enough to generate the tubes from only 3, 6 and 9 atoms, respectively; the coordinates of these atoms are given, thus completing determination of the conformations of the tubes. In Section 3 some of many symmetry based physical properties of the nanotubes are discussed: conserved quantum numbers and band degeneracies, normal modes, second-rank tensors and potentials.

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## 2 Symmetry of the $MS_2$ nanotubes

When a molecular monolayer exhibiting trigonal symmetry is folded up, the obtained tube is a quasi-1D structure translationally periodic in the direction of tube axis and its Euclidean symmetry is described by the line group [5], as well as the reported 3R and 2Hb polytypes tubes, built of two and three S-M-S layers. Therefore, after a brief review of the line groups, the geometry of the structures (although still not synthesized) formed by rolling up a monolayer is considered first.

### 2.1 Line groups

Any quasi-1D system being translationally periodic (with period $a$) along one axis ($z$-axis, by convention) is a regular arrangement of elementary structural units conventionally called monomers. This arrangement is achieved by acting on one of the monomers by the operations forming the generalized translational group Z, which is either a screw axis $T_q^r(a)$ (here belongs the pure translational group $T_q^0(a)$)) or a glide plane $T_c(a)$ group. Also, the monomer itself may have some point group symmetry [6]. Only those point operations leaving the $z$-axis invariant are compatible with the 1D translational periodicity, meaning that the maximal axial subgroup P of the monomer point group should be combined with Z to get full symmetry line group. Namely, the candidates for P are groups $C_n$, $S_{2n}$, $C_{nh}$, $C_{nv}$, $D_n$, $D_{nd}$, $D_{nh}$, where $n = 1, 2, \ldots$ is the principal rotational axis order. Altogether there are 13 infinite families
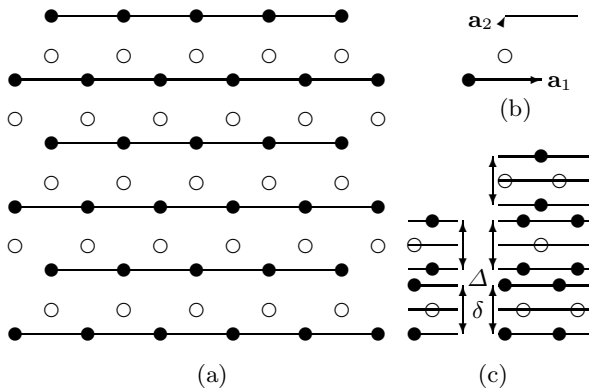
**Fig. 1.** (a) Perpendicular projection of the monolayer S-M-S ($\circ$ =M, $\bullet$ =S). (b) The elementary cell of the monolayer contains two overlapping sulfur and one transition metal atom. (c) Single layers of the 2Hb and 3R polytypes.

of the line groups $\mathsf{L} = \mathsf{ZP}$ differing in type of either $\mathsf{Z}$ or $\mathsf{P}$, and with $n$, $q$ and $r$ enumerating groups within each family. This means that each element of a line group is of the form $g = z^t C_n^s P$ ($t = 0, \pm 1, \ldots, s = 0, 1, \ldots, n-1$), where the screw axis $\mathsf{T}_q^r(a)$ is generated by $z = (C_q^r | \frac{na}{q})$ (Koster-Seitz notation), while in the glide plane case $z = (\sigma_v | \frac{a}{2})$; $C_n$ is the principle axis rotation of the point group and $P$ is some of the remaining point group operations $U$ (the rotation for $\pi$ around the horizontal axis), $\sigma_v$ and $\sigma_h$ (vertical and horizontal mirror planes). Monomer is only a part of an elementary cell: the translational period of $\mathsf{T}_q^r(a)\mathsf{P}$ and $\mathsf{T}_c(a)\mathsf{P}$ contains $q/n$ and 2 monomers, respectively.

Note that the value of $r$ is not unique: together with $r$ also $r + m\frac{q}{n}$, $m = \pm 1, \pm 2, \ldots$ lead to the same line group. The ambiguity is resolved by convention choosing $r$ to be coprime with $q$ (alternatively, the minimal $r$ may be used, when it is coprime to $q/n$).

## 2.2 Monolayered tubes

The monolayer M-S-M [1] consists of a pair of parallel sulfur planes at a distance $\delta \approx 6$ Å, bisected by the transition metal plane (Fig. 1). All three planes are of the same trigonal lattice, with the basis vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ of equal length $a_0 \approx 3$ Å. While the sulfur atoms in the different planes are exactly one above another, the metal atoms are between the centers of the sulfur triangles. Thus the elementary cell of the layer contains two S atoms at $(0,0)$ (at the heights 0 and $\delta$) and the transition metal atom at $(1/3, 1/3)$ (at the height $\delta/2$). This layer has trigonal symmetry of the diperiodic group Dg78 = p$\bar{6}$m2 (symorphic, with the isogonal group $\mathsf{D}_{3h}$; the horizontal mirror plane coincides with M-plane) [7].

The monolayered tube $(n_1, n_2)$ is formed when this lattice is rolled up in such a way that the *chiral vector* $\mathbf{c} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2$ becomes a horizontal circle on the tube. Analogously to the carbon nanotubes, the *chiral angle* $\theta = \arctan \frac{\sqrt{3} n_2}{2n_1 + n_2}$ is the angle between the lattice vector $\mathbf{a}_1$ and the chiral vector. Again, the chiral angles from the interval $[0, \pi/6]$ suffice for the description of all the tubes,

since those with the angles from $[\pi/6, \pi/3]$ are their optical isomers (the other angles result in the same tubes, due to symmetry of the 2D lattice). Tubes $(n, 0)$, having zero chiral angle are called *zigzag* ($\mathcal{Z}$ for short), the armchair ($\mathcal{A}$) tubes are $(n, n)$ ones (with $\theta = \pi/6$), while all others are referred as the *chiral* ones ($\mathcal{C}$, $n_1 > n_2 > 0$, with $\theta \in (0, \pi/6)$).

The finite thickness of the monolayer results in different distortions of the interior and exterior parts of the tube. It is proposed [8] that the transition metal cylinder is purely rolled up, while the interior and exterior sulfur ones are additionally shrunken and stretched, respectively, such that their radii are less (greater) than the metallic one for $\delta/2$. Although diameter, as well as many other quantitative properties (such as elastic energy or the dispersion relations), of the tube depends on the described distortions, the symmetry group, and consequently the symmetry based properties considered here are not affected by this.

The diameter of the non-distorted cylinder is $|\mathbf{c}|/\pi$ (the length of the chiral vector is $\sqrt{n_1^2 + n_1 n_2 + n_2^2} a_0$). Thus, the interior $D_{\text{in}}$ (sulfur) diameter is

$$D_{\text{in}} = \sqrt{n_1^2 + n_1 n_2 + n_2^2} a_0 - \delta, \tag{1}$$

and it will be mainly used in the following. The outer diameter is obviously $D_{\text{out}} = D_{\text{in}} + 2\delta$.

The symmetry groups of the MS$_2$ tubes are found by the procedure established for the carbon nanotubes [4]. It is based on the fact that roto-translational tube symmetries emerge from translational periodicity of the unfolded 2D layer. The only modification is the odd order of the diperiodic group principle axis (due to the mutual displacement of the sulfur and metallic sub-lattices), resulting in absence of the $U$ axis. Here, only the results, obtained by an easy modification according to this difference, will be given. To this end, at first the number of the 2D lattice cells in the elementary cell of the tube $(n_1, n_2)$ is found to be

$$q = 2\frac{n_1^2 + n_1 n_2 + n_2^2}{n\mathcal{R}} = \frac{2|\mathbf{c}|^2}{\mathcal{R}a_0^2}, \tag{2}$$

where $n$ is the greatest common divisor of $n_1$ and $n_2$, while $\mathcal{R} = 3$ if $n_1 - n_2$ is multiple of $3n$, and $\mathcal{R} = 1$ otherwise. Note that $3q$ is the number of atoms in the elementary cell of the tube.

The symmetry group of the chiral tube $(n_1, n_2)$ is the first family line group

$$\mathsf{L}_{\mathcal{C}} = \mathsf{T}_q^r(a)\mathsf{C}_n, \quad a = \sqrt{\frac{3q}{2n\mathcal{R}}} a_0, \tag{3}$$

$$r = \frac{n_1 + 2n_2 - (\frac{n_2}{n})^{\varphi(\frac{n_1}{n}) - 1} q\mathcal{R}}{n_1 \mathcal{R}} \pmod{\frac{q}{n}}$$

(the Euler function $\varphi(x)$ gives the number of coprimes not greater than $x$). Each cylinder is one orbit (the set of atoms generated from one of them by the group transformation) of the $a_1$ type [5]. The interior sulfur cylinder

is used to fix the coordinate system, choosing the orbit representative atom on the $x$-axis. Thus the cylindrical coordinates of the orbit representatives are

$$\left(\frac{D_{\text{in}}}{2},0,0\right), \quad \left(\frac{D_{\text{in}}+\delta}{2},\phi_0,z_0\right), \quad \left(\frac{D_{\text{in}}}{2}+\delta,0,0\right), \tag{4}$$

for interior sulfur, metal and outer sulfur, respectively. Here, $\phi_0 = \pi \frac{n_1+n_2}{n_1^2+n_1n_2+n_2^2}$, $z_0 = \frac{a_0}{2\sqrt{3}}\frac{n_1-n_2}{\sqrt{n_1^2+n_1n_2+n_2^2}}$. This orbit has a trivial stabilizer (set of the group elements leaving the representative atom invariant), meaning that at each cylinder the atoms may be enumerated by the group elements. Precisely, the action of the general element of the group (3) on the point given by the cylindrical coordinates is

$$(C_q^r|\tfrac{q}{n}a)^t C_n^s\,(\rho,\phi,z) = (\rho, \phi + 2\pi(\tfrac{rt}{q}+\tfrac{s}{n}), z + \tfrac{q}{n}ta). \tag{5}$$

Thus, any atom in the cylinder (orbit) is given by its orbit representative and pair $(t,s)$; its coordinates are given by (5) with the corresponding representative coordinates from (4) taken for $(\rho,\phi,z)$.

The symmetry group of the zigzag monolayered tube $(n,0)$ belongs to the eighth line group family:

$$\mathsf{L}_{\mathcal{Z}} = \mathsf{L}(2n)_n mc = \mathsf{T}_{2n}^1(\sqrt{3}a_0)\mathsf{C}_{nv}. \tag{6}$$

Again, each cylinder is single $b_1$ orbit, with the coordinates of orbit representatives given by (4), where $\phi_0 = \pi/n$ and $z_0 = \sqrt{3}a_0/6$. The stabilizer is $\mathsf{C}_{1v}$, meaning that the whole orbit can be generated by the chiral group (3), with $r = 1$ and $q = 2n$. The inner diameter is $D_{\text{in}} = na_0/\pi - \delta$.

For the armchair monolayered tube $(n,n)$ the symmetry is described by the fourth line group family:

$$\mathsf{L}_{\mathcal{A}} = \mathsf{L}(2n)_n/m = \mathsf{T}_{2n}^1(a_0)\mathsf{C}_{nh} \tag{7}$$

The cylinders are orbits of $b_1$ type generated by the atoms positioned as in (4), with $\phi_0 = 2\pi/3n$ and $z_0 = 0$. The stabilizer is $\mathsf{C}_{1h}$, and the orbit is effectively generated by the chiral group again. The inner diameter is $D_{\text{in}} = \sqrt{3}na_0/\pi - \delta$.

## 2.3 Single-layered 2Hb and 3R polytype tubes

Both $WS_2$ and $MoS_2$ crystallize in two forms (space groups P63/$mmc$ and R3$m$), differing in stacking of the monolayers along the perpendicular direction. The single layer of the hexagonal 2Hb polytype contains two monolayers positioned so that sulfur (metal) atoms of the second monolayer are above the metal (sulfur) atoms of the first one, *i.e.* the second monolayer is rotated for $\pi/3$ (around the perpendicular axis through S) and then translated for $(\mathbf{a}_1 + \mathbf{a}_2)/3$. A single layer of the 3R polytype consists of three monolayers: the second is translated for $(\mathbf{a}_1 + \mathbf{a}_2)/3$ with respect to the first (S atoms are moved above M atoms of the first monolayer), while the third one is translated for $2(\mathbf{a}_1 + \mathbf{a}_2)/3$ (its M atoms get above

the S atoms of the first layer). In both cases the distance between monolayers [1] is $\Delta \approx 2$ Å.

According to the experimental evidence, the walls of $MS_2$ tubes are the 2Hb or 3R polytypes single layers, manifesting high stretchability of the monolayers [8]. The nanotubes $(D_{\text{out}} < 0.1\,\mu\text{m})$ grow in the hexagonal 2Hb polytype, while the microtubes $(D_{\text{out}} > 2\,\mu\text{m})$ grow in rhombohedral 3R polytype [9]. Despite different space groups of crystalline polytypes, the layer's symmetry is the same symorphic diperiodic group Dg69 = p3m1, with isogonal point group $\mathsf{C}_{3v}$. In comparison to the monolayer Dg78, it does not have the horizontal mirror plane. When the layer is rolled up into the tube, such a plane produces no tube symmetry, meaning that the same line group is obtained for the monolayered and both polytype single layer tubes of the same chirality. Thus, the only difference is in the number of the orbits out of which these systems are built: while the monolayered tubes have $N = 3$ orbits, the single-layered 2Hb tube consists of $N = 6$ orbits, and the single-layered 3R tube of $N = 9$ orbits.

If the inner monolayer is taken as the referent one, *i.e.* its orbit representative atoms have coordinates (4), the atoms generating the additional three orbits of the 2Hb single-layered tube are positioned at (in the order from the inner to the outer orbits):

$$\left(\frac{D_{\text{in}}^{(2)}}{2},\phi_0,z_0\right), \quad \left(\frac{D_{\text{in}}^{(2)}+\delta}{2},0,0\right), \quad \left(\frac{D_{\text{in}}^{(2)}}{2}+\delta,\phi_0,z_0\right),$$

where, $D_{\text{in}}^{(2)} = D_{\text{in}} + 2\delta + 2\Delta$ is the inner diameter of the second monolayer. As for six additional orbit representative atoms of 3R tubes one finds

$$\left(\frac{D_{\text{in}}^{(2)}}{2},\phi_0,z_0\right), \quad \left(\frac{D_{\text{in}}^{(2)}+\delta}{2},2\phi_0,2z_0\right),$$

$$\left(\frac{D_{\text{in}}^{(2)}}{2}+\delta,\phi_0,z_0\right),$$

for the middle monolayer; the coordinates for the third monolayer having the inner diameter $D_{\text{in}}^{(3)} = D_{\text{in}}+4\delta+4\Delta$, are:

$$\left(\frac{D_{\text{in}}^{(3)}}{2},2\phi_0,2z_0\right), \quad \left(\frac{D_{\text{in}}^{(3)}+\delta}{2},0,0\right),$$

$$\left(\frac{D_{\text{in}}^{(3)}}{2}+\delta,2\phi_0,2z_0\right).$$

These data refer to the arbitrary chiral direction $(n_1,n_2)$. In the special cases of zigzag and armchair directions, the results are obtained by substituting the values given for the corresponding monolayers for $\phi_0$ and $z_0$.

## 3 Symmetry determined properties of $MS_2$ nanotubes

Many physical properties are based on symmetry. Also, the symmetry enables applications of the powerful group

theoretical techniques in solving various physical problems. In this paper, the presented symmetry classification of the transition metal dichalcogenide tubes is used to derive some of their physical properties determined by symmetry, postponing the applications to various symmetry based calculations (band structures, selection rules, etc.).

## 3.1 Quantum numbers and band degeneracies

Symmetry determines quantum numbers extensively used in almost all problems (*e.g.* selection rules, band assignment). Translational periodicity is reflected in the conserved quasi-momentum $k$, taking on the values from the 1D Brillouin zone $(-\pi/a, \pi/a)$. For the armchair tubes, it can be taken from the irreducible domain $[0, \pi/a]$ only [6], since the horizontal mirror plane $\sigma_h$ makes $k$ and $-k$ equivalent. The $z$-component of the quasi-angular momentum $m$ is the quantum number due to the symmetry of the isogonal rotations: since the order of the principle axis of isogonal point group is $q$, $m$ runs over the integers from the interval $(-\frac{q}{2}, \frac{q}{2}]$ and characterizes the nanotube energy bands. In the zigzag tubes, the vertical mirror plane makes $m$ and $-m$ equivalent, thus reducing this interval to its non-negative half. Since all of the nanotubes are non-symorphic, the isogonal group is not a subgroup of the symmetry group; consequently some of its rotations are not symmetries of the system at all, and the quantum number $m$ is not a conserved quantity. Nevertheless, these quantum numbers are frequently used, at the cost of more complicated selection rules.

Alternatively, the conserved quantum numbers of helical ($\tilde{k} \in [0, q\pi/na]$) and pure angular quasi momenta ($\tilde{m}$, taking on the integer values from the interval $(-\frac{n}{2}, \frac{n}{2}]$) can be used. The former is related to the momentum conjugated to the screw axis generated helix, and it obviously incorporates a part of the angular momentum. The remaining part $\tilde{m}$ is conserved, since it corresponds to the order $n$ principle axis of symmetry of the tubes.

The zigzag (armchair) tubes have an additional quantum number A/B (*i.e.* $+/-$) of parity with respect to the vertical (horizontal) mirror plane. Due to this extra symmetry the two-dimensional irreducible representations appear, *i.e.* the degeneracy of the energy bands can be at most double or if the time-reversal symmetry of the (spin-independent) Hamiltonian is taken into account, the maximal degeneracy is fourfold [10].

Concerning the chiral tubes, their energy bands are nondegenerate (as long as the time-reversal symmetry is not included).

## 3.2 Normal modes

The classification of the vibrational bands depends only on the symmetry group and the orbits out of which the system is formed. The general classification has been performed already for all orbit types of the line groups [5]. Since the considered tubes are decomposed to the orbits in the previous section, the results for each of the found orbits are to be summed only.

All the tubes considered here consist of a finite number of the orbits of the same type. The symmetry group and (henceforth) orbit type depend on the chiral vector, not on the polytype (monolayer, 2Hb or 3R): $a_1$ orbit for the chiral tubes and $b_1$ orbits for zigzag and armchair tubes (recall that these tubes have different symmetries; *i.e.* while for the zigzag tube the $b_1$ orbit representative lay in the vertical mirror plane, for the armchair tube it is in the horizontal plane). On the contrary, the number of orbits is determined by the polytype: there is $N = 3, 6, 9$ orbits in the monolayered, 2Hb, 3R tubes, respectively. Thus the first step in a lattice dynamics study can be performed by the classification of the vibrational bands, giving the band quantum numbers. Taking the dynamical representation decomposition [5] for the found orbit types, the phonons (normal modes) are classified. For the chiral tubes one obtains

$$D_{\mathcal{C}}^{\text{dyn}} = 3N \sum_{\tilde{k}} \sum_{\tilde{m}} {}_{\tilde{k}}A_{\tilde{m}}, \tag{8}$$

where the summation is performed over $\tilde{k} \in (-\frac{q\pi}{na}, \frac{q\pi}{na}]$ and integers $\tilde{m} \in (-\frac{n}{2}, \frac{n}{2}]$. It follows that there are $3Nn$ vibrational bands assigned by the quantum number $\tilde{m}$. The representations ${}_{\tilde{k}}A_{\tilde{m}}$ are one-dimensional, meaning that the bands are non-degenerate. Still, since the Hamiltonian is real, the time reversal symmetry leads to the double degeneracy of the bands over $\tilde{k} \in (0, \frac{q\pi}{na}]$: the energies of the phonons with quantum numbers $(\tilde{k}, \tilde{m})$ and $(-\tilde{k}, -\tilde{m})$ are equal.

The corresponding decompositions for the zigzag and armchair tubes are:

$$D_{\mathcal{Z}}^{\text{dyn}} = N \sum_{k \in (-\frac{\pi}{a}, \frac{\pi}{a}]} \Big[ 2_k A_0 + 2_k A_n + {}_k B_0 $$
$$ + {}_k B_n + N \sum_{m=1}^{n-1} {}_k E_m \Big], \tag{9}$$

$$D_{\mathcal{A}}^{\text{dyn}} = N \sum_{m=-n+1}^{n} \left( {}_0 A_m^- + 2_0 A_m^+ \right) $$
$$ + 3N \sum_{k \in (0, \frac{\pi}{a})} \sum_{m=-n+1}^{n} {}_k E_m + 3N \sum_{m=1}^{n} {}_\pi E_m. \tag{10}$$

Here, ${}_k A_m$ and ${}_k B_m$ correspond to non-degenerate $m$-bands of different vertical mirror parity, while ${}_k E_m$ denotes the double degenerate band. As for the armchair tubes, the second term classifies the double degenerate bands, while the terms with $k = 0$ and $k = \pi$ give insight into the bands topology (touching at the Brillouin zone boundaries) and horizontal mirror parity of $k = 0$ modes.

These decompositions can be used to simplify further the vibrational band calculations by standard methods. The obtained bands are automatically assigned by good

quantum numbers so that Raman and IR spectra can be directly extracted by selection rules [11], as the relevant line group is found.

### 3.3 Second rank tensors

As the symmetry classification of the $MS_2$ tubes has been completed the general matrix forms of the symmetric polar and axial second-rank tensors for systems with line group symmetry [4] can be used to predict many of the physical properties. Here the optical activity of the isolated nanotubes will be analyzed. In order to avoid influence of the other effects, birefringence and anisotropy of absorption, only the activity along the optical axis is discussed. The optically active medium rotates the plane of polarization of a linearly polarized incident light beam incoming along the optical axis, defined by the unit vector $\mathbf{e} = (e_1, e_2, e_3)$, through an angle $\sum_{i,j} e_i e_j a_{ij}$ per unit length, where $a_{ij}$ denote optical activity tensor elements. As this tensor is an axially symmetric second rank tensor, from the general axial tensor form [4] only the symmetric part is to be taken. The general form of the dielectric tensor, *i.e.* a polar symmetric second-rank tensor is needed to predict the spatial orientation of the optical axes.

The general form both of the tensor of the optical activity and of the dielectric tensor for the chiral tubes with symmetry $\mathsf{T}_q^r \mathsf{C}_n$, for $q > 2$ what encounters all the realistic cases, is given by the matrix:

$$\mathsf{B} = \begin{pmatrix} b_\perp & 0 & 0 \\ 0 & b_\perp & 0 \\ 0 & 0 & b_\parallel \end{pmatrix}.$$

As the optical activity tensor does not vanish, the chiral tubes are expected to be optically active. The pair of equal eigenvalues of the dielectric tensor single out the tube axis as the optical axis. The polarization plane is rotated through an angle proportional to the value of $a_\parallel$. Since quasi-two-dimensional transition metal dichalcogenide layers are optically inactive, the value of $a_\parallel$ continuously diminishes with the tube diameter. As has been already mentioned, the tubes $(n_1, n_2)$ and $(n_2, n_1)$ are the optical isomers rotating the polarization of the incoming light in the mutually opposite directions (through equal angles).

On the other side, zigzag and armchair tubes are optically inactive as, due to the symmetry, their second-rank axial tensors vanish.

### 3.4 Potentials

Potential $V(\mathbf{r})$ in a nanotube must be invariant under the symmetry transformations: $V(\mathbf{r}) = V(l^{-1}\mathbf{r})$, for all $l \in \mathsf{L}$, where $\mathsf{L}$ is the symmetry group of the tube considered. This property leads to the quite restrictive conditions on the general form of the potential function $V(\mathbf{r})$. The translational (generated by $(I|a)$) and rotational (generated by $C_n$) symmetries, manifested as $V(\rho, \varphi, z) = V(\rho, \varphi, z - a)$

and $V(\rho, \varphi, z) = V(\rho, \varphi - \frac{2\pi}{n}, z)$ enable the Fourier expansion over coordinates $\varphi$ and $z$.

The screw axis generator $(C_q^r | \frac{na}{q})$ imposes the condition $V(\rho, \varphi, z) = V(\rho, \varphi - \frac{2\pi r}{q}, z - \frac{na}{q})$. This restricts the general form of the potentials produced by a chiral tube to the Fourier expansion

$$V_{\mathcal{C}}(\rho, \varphi, z) = \sum_{\substack{K, M = -\infty \\ (Mr = -K \bmod \frac{q}{n})}}^{+\infty} \alpha_K^M(\rho) e^{inM\varphi} e^{i(2\pi/a)Kz} \quad (11)$$

(only the terms satisfying the braced equation are summed).

As for the zigzag and armchair tubes $q = 2n$ and $r = 1$, this means that the summation in (11) is performed only over the terms with $K$ and $M$ of the same parity. The additional symmetries are manifested as relations between the coefficients $\omega_K^M(\rho)$, $\epsilon_K^M(\rho)$. The invariance of the potential of the zigzag (armchair) tubes under the vertical (horizontal) mirror plane $\sigma_\mathrm{v}$ ($\sigma_\mathrm{h}$) means $V(\rho, \varphi, z) = V(\rho, -\varphi, z)$ (*i.e.* $V(\rho, \varphi, z) = V(\rho, \varphi, -z)$); this leads to the general form of the potential:

$$V_{\mathcal{Z}}(\rho, \varphi, z) = \sum_{\substack{K = -\infty \\ \mathrm{odd}}}^{\infty} \sum_{\substack{M = 1 \\ \mathrm{odd}}}^{\infty} \omega_K^M(\rho) \cos(Mn\varphi) e^{i(2\pi/a)Kz}$$
$$+ \sum_{\substack{K = -\infty \\ \mathrm{even}}}^{\infty} \sum_{\substack{M = 0 \\ \mathrm{even}}}^{\infty} \epsilon_K^M(\rho) \cos(Mn\varphi) e^{i(2\pi/a)Kz};$$

$$V_{\mathcal{A}}(\rho, \varphi, z) = \sum_{\substack{K = 1 \\ \mathrm{odd}}}^{\infty} \sum_{\substack{M = -\infty \\ \mathrm{odd}}}^{\infty} \omega_K^M(\rho) e^{inM\varphi} \cos\left(\frac{2\pi}{a} Kz\right)$$
$$+ \sum_{\substack{K = 0 \\ \mathrm{even}}}^{\infty} \sum_{\substack{M = -\infty \\ \mathrm{even}}}^{\infty} \epsilon_K^M(\rho) e^{inM\varphi} \cos\left(\frac{2\pi}{a} Kz\right).$$

The obtained potentials can be further specified. When the Taylor expansion of $\alpha_K^M(\rho), \omega_K^M(\rho), \epsilon_K^M(\rho)$ is performed the terms of the same order in $\rho$ should form the invariant polynomial of the relevant line group, *i.e.* these coefficients are polynomials over the integrity basis of the line group [4].

## 4 Concluding remarks

Geometry of the tubes is completely defined: line groups, number and type of orbits, coordinates of the atom representing orbits are specified generally, *i.e.* for the tubes of arbitrary chirality. In addition to the rotational, translational and screw axes symmetry of the $(n_1, n_2)$, $0 < n_2 < n_1$ tubes, the armchair and zigzag tubes are invariant under reflection in the mirror planes: the horizontal and the vertical one, respectively. This leads to the parities of their quantum states which now can be degenerate, in contrast to the chiral nanotube quantum states which (as far as the time-reversal symmetry is not considered)

are non-degenerate. Thus, the complete symmetry groups of the chiral, armchair and zigzag tubes are:

$$\mathsf{L}_{\mathcal{C}} = \mathsf{T}_q^r \mathsf{C}_n,$$
$$\mathsf{L}_{\mathcal{A}} = \mathsf{L}_{\mathcal{C}} + \sigma_{\mathrm{h}} \mathsf{L}_{\mathcal{C}} = \mathsf{T}_q^r \mathsf{C}_{n\mathrm{h}},$$
$$\mathsf{L}_{\mathcal{Z}} = \mathsf{L}_{\mathcal{C}} + \sigma_{\mathrm{v}} \mathsf{L}_{\mathcal{C}} = \mathsf{T}_q^r \mathsf{C}_{n\mathrm{v}}.$$

Note that the parameters $q$ and $r$ of the helical group have the same form as the ones of the corresponding single-wall carbon nanotubes [4].

The derived symmetry classification of the inorganic $MS_2$ nanotubes is used to discuss some of their physical properties. First, the good quantum numbers, characterizing the nanotube quantum states are found: the translational, helical and rotational symmetries are reflected in the conserved quasi-momenta $k$, $\tilde{k}$ and $\tilde{m}$. The isogonal angular momentum $m$ is also used in combination with $k$, although it is not a conserved quantity. The ranges of these momenta are given. The vertical (horizontal) mirror plane of zigzag (armchair) tubes introduces the additional parity quantum numbers denoted by $A$ and $B$ ($+$ and $-$) for even and odd states, respectively.

The above enumerated quantum numbers are used in assignation and *a priori* degeneracy prediction of electronic and vibrational bands. No geometry caused degeneracy is expected for the chiral tubes, while for the zigzag and armchair tubes double degeneracy in the interior of the irreducible domain is obligate. Besides the time reversal symmetry, which when appropriate, doubles these degeneracies, the diameter of the tube is also relevant in this context. Namely, the diperiodic symmetry of the single 2Hb and 3R layers (as well as that of monolayer) imposes six-fold degeneracy of the bands in the interior of the 2D Brillouin zone. Thus, for the large diameter tubes several (six for chiral and three for achiral ones) bands become quasi degenerate. This effect should be observable in microtubes.

Also, the tensors of optical activity and dielectric permeability are studied. The optical activity of the chiral tubes and inactivity of the armchair and zigzag ones is demonstrated. In fact, these results are typical, meaning that the same forms must be obtained for any symmetric axial (polar) second rank tensor.

Finally, the general forms of the potentials in nanotubes are given, thus enabling the generalization of the Bloch theorem to the line group symmetry: by multiplication of the invariant potential functions with irreducible representation matrix elements, all the symmetry allowed covariants and wave functions can be obtained.

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