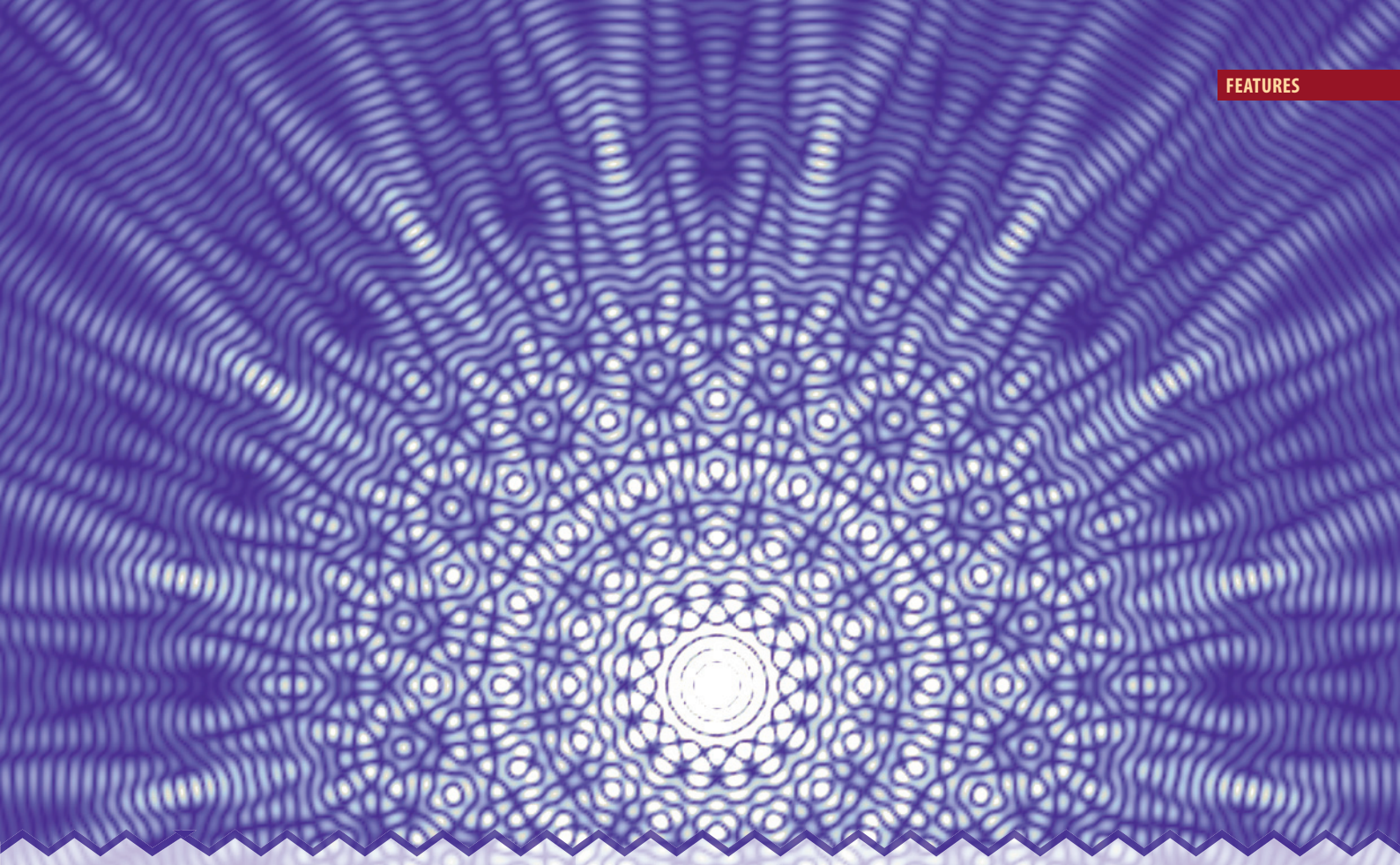

SYMMETRY OF QUASI ONE-DIMENSIONAL SYSTEMS: LINE GROUPS AND APPLICATIONS

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Many of the interesting properties of stereoregular polymers, nanotubes and other nanowires exhibit quasi one-dimensionality and regularity. These specific configurations are determined by their symmetry described by line groups. Deep physical consequences of this type of symmetry are illustrated by using modified group projector technique.

More than 30 years ago it was understood that low-dimensional systems have many features which distinguish them from traditional crystals. *New physics is expected in low-dimensional matter*, was the prophetic formulation of Nobel prize winner Vitaly Ginzburg. Indeed, most contemporary condensed matter physics is focused on nanotubes, polymers, graphene and other nanowires and layers. An avalanche-like growth in research overflowed the other fields under the fashionable names nanoscience, nanotechnology, nanobiotechnology, *etc.*, all stressing the nanoscale. The interrelated classical sciences and high-tech breakthroughs are probably the first example in the history of civilization of how the developments of fundamental and applied knowledge are interrelated through an endless series of feed-backs.

Wigner's work in the middle of the 20th century promoted symmetry, perhaps the deepest concept of science and philosophy, to one of the cornerstones and the most fruitful tool of quantum physics. It is precisely through quantum mechanics, inevitable on the nanoscale, that it penetrates physics of low dimensions. The mathematics describing symmetry is group theory, and quasi one-dimensional (Q1D) systems are related to line groups.

Some of them were first mentioned in 1923, with several important results ever since. However, following growing interest for polymers, the systematic investigation of

▲ Diffraction k-space equatorial perpendicular cross section of (8,8) carbon nanotube

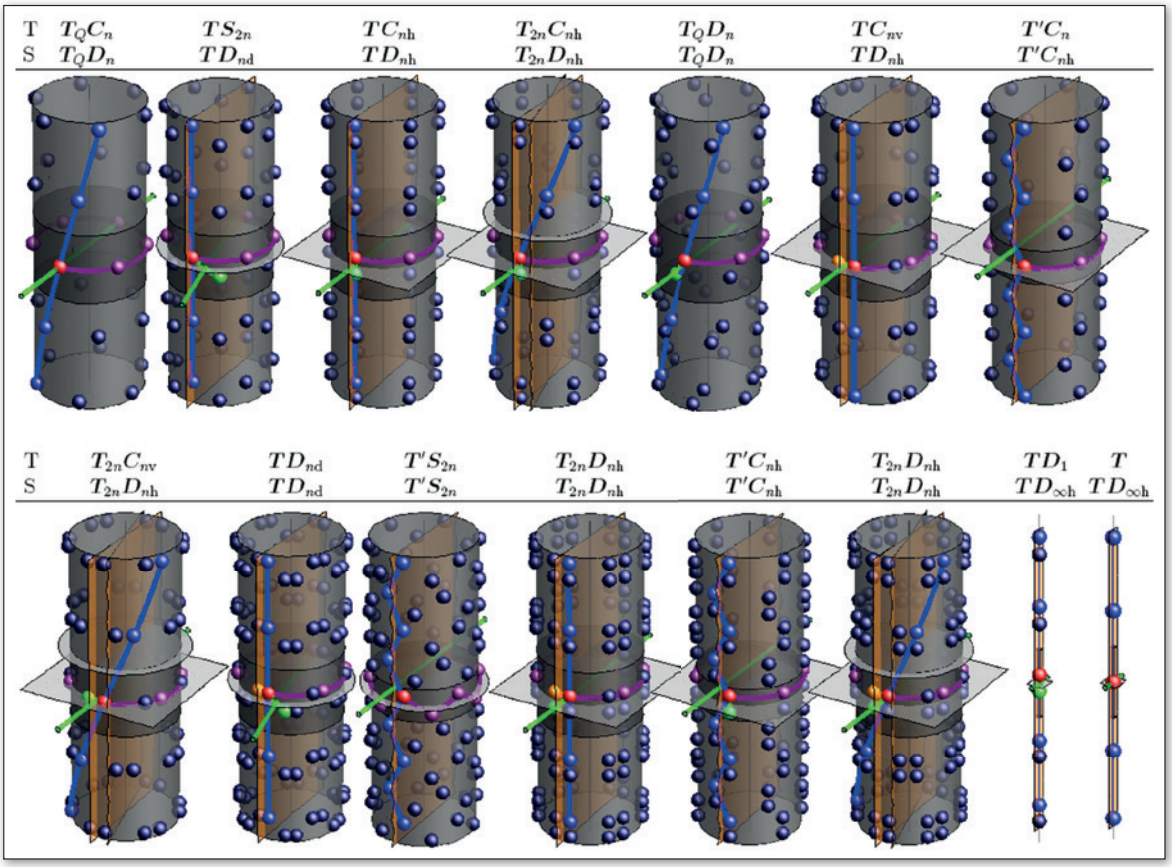
line groups for physical applications did not start until 1977 at the Faculty of Physics, University of Belgrade, by Božović, Vujičić and Herbut [1], and their coworkers (presently NanoLab, www.nanolab.rs); a synthesis of the existing results was given in 2010 [2]. Simultaneously, the modified group projector technique (MGPT), enabling full symmetry calculations, and computer code POLSym, suited for symmetry assisted research of quasi one-dimensional systems, were developed [2].

Line groups

Natural insight into line groups arises from a physical point of view. The common characteristic of Q1D systems and subsystems of 3D solids is their great length compared to width. This determines the direction along which the basic constituents, identical *monomers*, are regularly repeated (z-axis). Accordingly, their geometrical symmetries arise in two different ways: *intrinsic symmetry* of monomer itself, and symmetry of the regular *arrangement* of monomers. This has far-reaching physical consequences.

Firstly, all line groups are obtained by independent classification of possible symmetries of monomers and symmetries of arrangements. The monomer symmetry is one of axial point groups (groups of transformations that leave z-axis invariant). These are $\mathbf{C}_n$ (successive rotations C_n by $2\pi/n$ around z-axis, n=1,2,…), $\mathbf{S}_{2n}$, $\mathbf{C}_{nh}$, $\mathbf{C}_{nv}$, $\mathbf{D}_n$ (which combine $\mathbf{C}_n$ with rotation by π/n followed by horizontal mirror reflection, horizontal and vertical mirror plane and rotation U by π around x-axis, respectively) and $\mathbf{D}_{nd}$ and $\mathbf{D}_{nh}$ (vertical mirror reflection combined with $\mathbf{S}_{2n}$ and $\mathbf{C}_{nh}$). The arrangement of monomers is described by *generalized translations*, being either glide plain or screw-axis. These are generated by $(\sigma_v|f)$ and $(C_Q|f)$, vertical mirror and rotation by $2\pi/Q$ around z-axis (Q is a real number not less than 1), followed by translation by f along this axis. Thus, counting pairs of compatible monomer and arrangement symmetry groups, all of 13 infinite families of line groups are found. Acting on a single point, they produce two types of 1D chains and 13 types of nonlinear Q1D elementary systems, from which all Q1D systems are built (Fig. 1). Magnetic and spin groups, Jahn-Teller activity, generalized Bloch functions, symmetry of carbon and all other nanotubes, diffraction patterns, are some of the important standard symmetry tools already derived for line groups. All these results greatly facilitate analysis and prediction of physical properties of Q1D systems.

It should be emphasized that only for rational Q the compound has translational symmetry, while in other cases it has not - it is *incommensurate*. Only Q1D systems may be incommensurable. This makes them essentially different from two- and three-dimensional ones, as periodicity along two or three directions leads to translationally periodic crystalline structures. For example, numerical predictions show that in single-walled carbon nanotubes translational periodicity is broken by a small torsion. This is also the reason why there are continuously many line groups, in contrast to the finite number of crystallographic ones (rod groups).



▸ **FIG. 1:** Types of building blocks of Q1D systems. Generating line group and full symmetry group are given in the upper row. The action of the generalized translations is depicted in blue (helices for screw-axes and zig-zags for glide planes) and that of C_n and S_{2n} in purple; The U –axis and the horizontal and vertical mirror (roto-reflectional and glide) planes are green, gray and orange, respectively. The single monomer is denoted by dark gray.

Among the deepest physical consequences of symmetry are conservation laws. The described factorization shows that the conserved quantities in Q1D systems are introduced separately from the two parts of symmetry. While axial point groups build in z-component of angular momentum $\tilde{m}$, generalized translations contribute by quasi helical momentum $\tilde{k}$, canonically conjugated to the helix generated by successive application of $(C_Q|f)$. Only in commensurate systems linear momentum is conserved as well. Thus, when the system is excited by an external perturbation carrying quantum numbers $\tilde{k}$ and $\tilde{m}$, the difference between helical and angular momenta in initial and final state must be $\tilde{k}$ and $\tilde{m}$. When the symmetry group involves mirror planes or U symmetries, there are additional conservation laws.

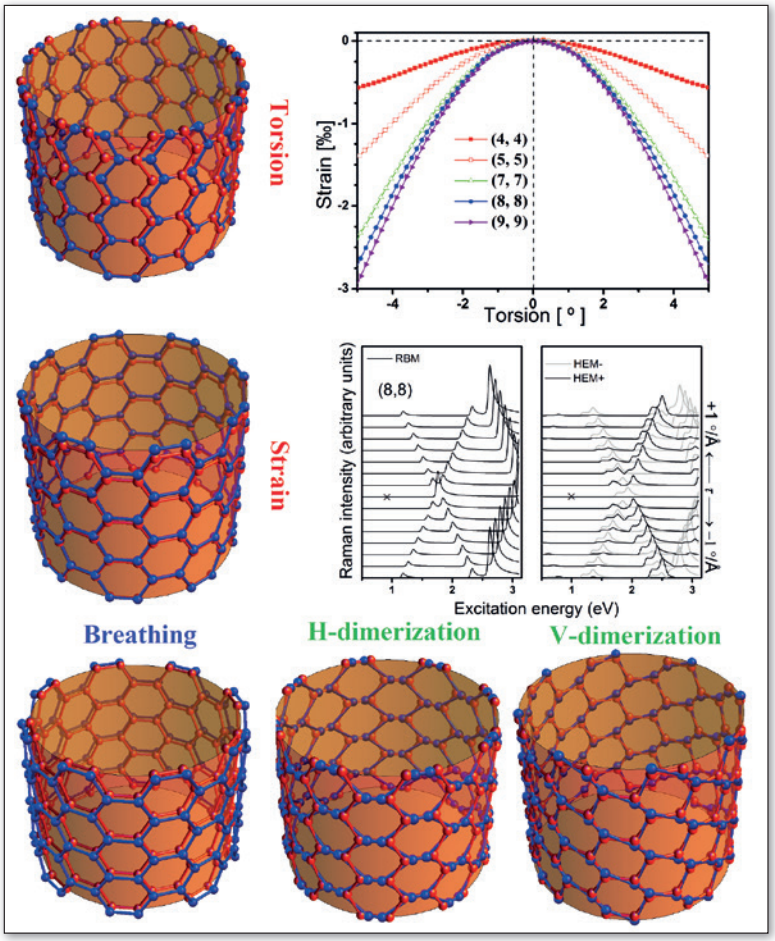
Carbon nanotubes and symmetry

Since their discovery carbon nanotubes have been in the focus of material science, with unique characteristics applicable in various fields of technology. Nanotubes are highly symmetric, to the extent that their symmetry group, completely defined through the line groups [3], generates the whole nanotube from a single atom. Thus, only symmetry and properties of the atom determine all properties of the nanotube. This is fruitfully and efficiently used in research [2,4].

Symmetries of the nanotubes are combined from $(C_Q|f)$, C_n (Q, n and f depend on the particular nanotube), U and vertical mirror reflection in achiral cases. As MGPT reduces calculations to the single atom, a stable configuration is obtained by relaxation (of the rolled graphene ribbon) over three coordinates (ρ, φ_0, z_0) of that atom, and continual line group parameters Q and f. Some nanotubes are incommensurate [5]. Deviations of the same parameters are deformations without breaking symmetry (Fig. 2): breathing (changing of diameter), horizontal and vertical dimerization (opposite displacements of the neighboring atoms), torsion and stretching. For stable and deformed configurations electronic and phonon energy bands and many other properties are easily found [6]. Deformations have an influence on conduction, optical and Raman spectra, which are interesting for applications. For example, optical absorption can be tuned by torsion, and some tubes can be used as optical sensors covering the whole visible spectrum.

Super slippery double-walled nanotubes

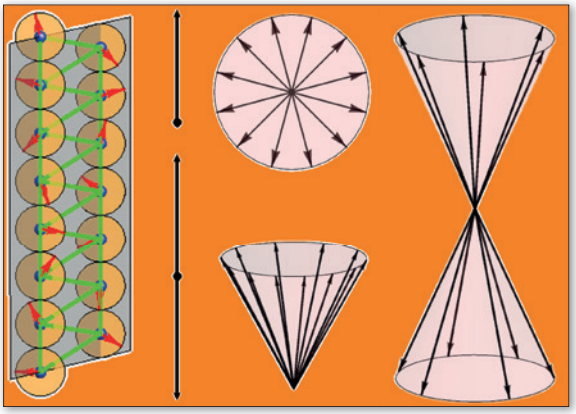
Despite being huge, symmetry groups of different nanotubes are highly incompatible, with only few common elements. Thus, symmetry of double- and multi-walled nanotubes is drastically diminished, frequently to a point group only. An amazing consequence is reduced interaction between the walls. The double-wall nanotube W@W' consists of coaxially positioned single-wall tubes, with line groups $\boldsymbol{L}$ and $\boldsymbol{L}'$. Its total symmetry $\boldsymbol{L}_{W@W'}$ is the intersection of $\boldsymbol{L}$ and $\boldsymbol{L}'$. If one wall is fixed, their relative positions are described by the angle Φ of rotation and vertical displacement Z of the other one. The energy of interaction of the walls, $E(\Phi,Z)$, is the sum of the pairwise interactions over atoms from the two walls. It is invariant under the group $\boldsymbol{L}_0$ of all pairs of transformations, one from $\boldsymbol{L}$ and one from $\boldsymbol{L}'$. As (Φ,Z) is not changed when an element from $\boldsymbol{L}_{W@W'}$ is applied to both walls, those pairs changing (Φ,Z) form a subgroup $\boldsymbol{L}_V$, with the number of elements equal to the ratio of the numbers of elements in $\boldsymbol{L}_0$ and $\boldsymbol{L}_{W@W'}$. Thus, the symmetry of interaction $\boldsymbol{L}_V$ exactly measures the *breaking of symmetry* produced by the interaction. Applied to any pair (Φ,Z) it generates equi-energetic positions. For incommensurate periods of walls $\boldsymbol{L}_V$ is large enough (bihelical [2]) to make $\boldsymbol{L}_{W@W'}$ finite: equi-energetic positions are continual along Z, and $E(\Phi,Z)$ is constant along Z. Walls are super slippery as their mutual translation costs no energy. The same effect cannot be achieved for mutual rotation, as Q and Q' are rational. Still, the results of relaxation [5] open also this possibility, particularly important for nanomachines.



▲ **FIG. 2:** Deformations that do not break symmetry. Stable configuration of the armchair (8,8) nanotube is red, the deformed configuration is blue. Torsion induces strain (effect shown in upper panel for series of armchair nanotubes), and affect electro-optical: torsions (from -1 to +1 degree per Angstrom) change Raman excitation profiles of radial breathing (RBM) and high energy (HEM), central panel.

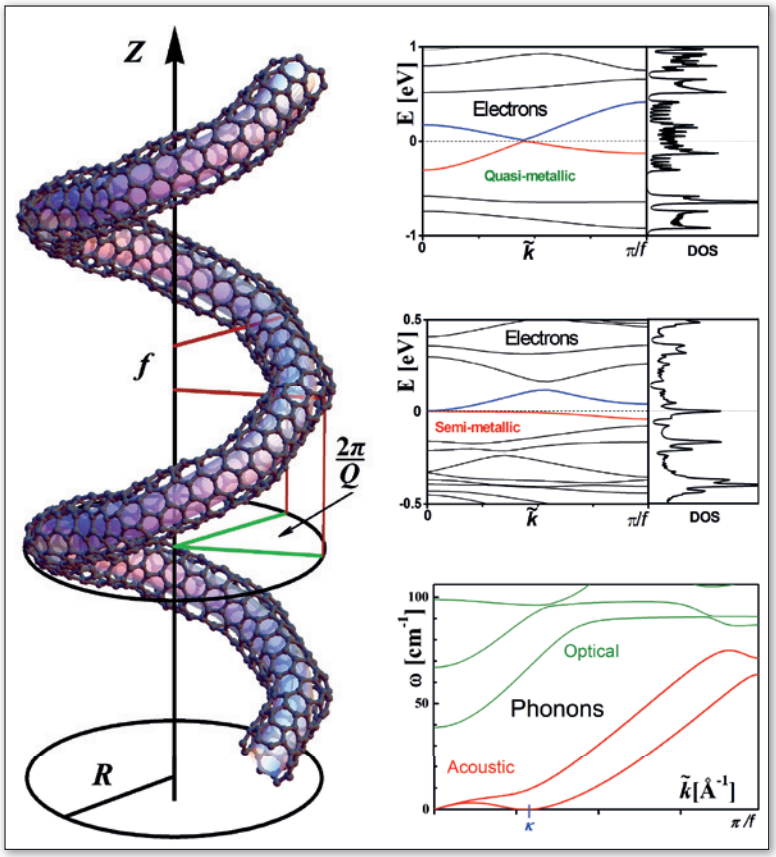
Magnetic properties

It is known that in Q1D spin systems and subsystems of 3D crystals (nanotubes, chains, spin-ladders), helimagnetic order, usually caused by Dzyaloshinskii-Moriya interaction, frequently appears. Symmetry provides the



▸ FIG. 3: Q1D spin arrangements. Described by spin line groups they are conical, with one or two opposite cones; special cases are linear (ferromagnets, antiferromagnets) and planar helical orderings. Left: planar helical spin arrangement on zig-zag Cu chain of $LiCu_2O_2$.

explanation: the χ^{xy}component of the spin susceptibility tensor χ (z-component of Dzyaloshinskii-Moriya vector), is scalar or pseudoscalar of line groups, and in the former case it can be in the Hamiltonian. In carbon nanotubes spin susceptibility is determined by RKKY interaction [7] and χ^{xy} is scalar. Particularly interesting are nanotubes composed of C^{13} isotope [8] with nuclear spin ½. The analysis shows that the susceptibility tensor has a continual number of symmetries described by the spin line groups $L_{\tilde{k}\tilde{m}\Pi}$. These are derived from the line groups (Fig. 3), associating change of the spin vectors to the geometrical action of geometrical transformations. This fact tremendously simplifies ground-state determination within the classical approximation, enabling to get interesting and very precise solution: helimagnetic spin line group order is expected, and it can be controlled by an applied gate.



▾ FIG. 4: Helically coiled carbon nanotube. Electron and phonon energy bands (right) do not cross. This causes semi-metallic and quasi-metallic conduction types and low acoustic branches ($\kappa=2\pi/Qf$) reflected in the small value of Young's modulus.

Helically coiled carbon nanotubes

The existence of helically coiled carbon nanotubes was predicted in 1993, and synthesized in 1994 [9]. With periodically arranged pentagons and heptagons they are incommensurate, with fifth family line group symmetry. All of them have $n=1$, leaving exclusively $\tilde{m}=0$ quasi angular momentum. Consequently, non-crossing energy band structures (Fig. 4) are immanent (Landau's rule). Thus, there are various conducting types, from semiconducting to metallic, including interesting quasi-metallic and semi-metallic with high and low mobility. The same property based on symmetry explains that super-elasticity is more pronounced in the tubes with high Q: acoustic branches, two of which connecting Γ point with $\tilde{k}=2\pi/Qf$, cannot cross optical branches, which is, due to lower sound velocity, reflected in elasticity modules and thermal conductivity.

Conclusion

Symmetry is one of the most profound ways to understand quasi one-dimensional regular systems and efficiently predict their properties at quantum level. This class of systems includes polymers and nanotubes, which are among the most interesting challenges of contemporary science. ■

About the Author

Milan Damnjanović is Professor of Quantum mechanics and Mathematical physics at Faculty of Physics, University of Belgrade. Together with collaborators of NanoLab (Prof. Ivanka Milošević, Prof. Tatjana Vuković, Dr Božidar Nikolić, Dr Saša Dmitrović , Dr Zoran Popović and Ph.D. studentsNataša Lazić and Marko Milivojević) he works on symmetry applications in quantum physics of quasi one-dimensional systems.

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