Conference paper

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Periodic law in chemistry and other sciences

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Abstract: Review of attempts to generalize the principle of periodic system to objects other than chemical elements in some areas of natural science, particularly in physics, molecular science and biology.

Keywords: biodiversity; chemical physics; chemical structures; chemistry education; electronic structures; isotopes; Mendeleev 150; particle synthesis; periodic table; phase diagrams; polycyclic aromatics; quantum chemistry; structure.

Introduction

Discovery of D.I. Mendeleev of the periodic system (PS) of chemical elements and the principle of periodicity made it possible to predict the properties of still unknown elements. The periodic law also influenced all those areas of natural science where there is a need for a natural classification of various natural objects. This especially affected the physics and chemistry of subatomic particles (for example, isotopes) and supramolecular objects (small molecules, clusters, etc.). It also influenced the biology, where the problem of rational taxonomy has always been very acute. Let us try to conduct – at least briefly – the review of the most striking attempts to generalize the principle of periodic system (below – PS) to objects other than chemical elements in some areas of natural science.

From atoms to ions and simple bodies

The periodicity of the properties of atoms is most clearly manifested when comparing the sizes of atoms and their ionization potentials. When passing from atoms to ions (differently charged cations or anions), both of these properties show a distinct periodicity, Fig. 1 [1]. Therefore, the PS principle is quite applicable to ions, and it is possible to construct a series of PS (separately for $X^+$ mono-cations, for $X^{2+}$ dication, $X^-$ monoanions, $X^{2-}$ dianions, etc.), isostructural to the PS of neutral atoms.

The properties of simple bodies, alas, do not obey the periodicity property. Atoms can form aggregates of various types, giving rise to the phenomenon of allotropy. Allotropes differ in the type of aggregation of atoms into molecules ($O_2$ and $O_3$, $S_2$ and $S_8$, $C_{60}$ and $C_{80}$), or (in)finite lattices (cf. red/white phosphorus, graphite/diamond, etc.). As a result, the macroscopic properties of simple bodies are very difficult to predict based only on PS of elements. The prediction of the melting point of the gallium allotrope is a fluke: on the phase diagram (P,T) there are two gallium allotropes with different melting points at different pressure.

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From atoms to nuclei and isotopes

One of the first PS of isotopes has been created by the Soviet physicist I.P. Selinov in 1934 [2]. Although different variants of PS of isotopes were proposed [2, 3], a large number of “cells” (~1700) impedes its visual (wall) tabular presentation. As a rule, isotopes are placed on bulky diagrams, combining the number of neutrons and protons (sometimes stable isotopes are labeled with a zigzag line) and divided into periods ending in nuclei with a “magic number” of nucleons [4], Fig. 2. If the basis of magic numbers for electrons in an atom is the sublevel capacity $2(2l + 1)$, then for nuclei this capacity is doubled (due to two types of nucleons – protons and neutrons). With the help of such substations, the search for “islands of stability” of super-heavy elements is being conducted.

From atoms to diatomic molecules

The consistent construction of molecules from atoms (with electrons in the field of a positively charged nuclear skeleton) underlies modern chemistry. The complexity of constructing the PS for even small molecules (for example, diatomic) is that, unlike atoms (where the pattern of filling with electrons of levels s, p, d, f… is
**Fig. 3:** (a) Hefferlin’s 4-D PS of diatomic molecules as a “product” of two PS of atoms. (b) An attempt to compose the same PS in the 3-dimensional form [1, 5].

**Fig. 4:** PS of the first 120 diatomic molecules according to Boldyrev. Closed-shell systems and radicals are marked in different colors [6, 7].
given in advance – as it is sometimes considered – by the rule \( n + 1 \), there is no similar pattern in molecules. (Filling order of levels can change when one atom is replaced by another.) Nevertheless, physicists are trying to build classification tables and look for patterns of changes in the properties of molecules in such “PS”. For example, R. Hefferlin (1929–2015) “multiplied” two PS of atoms (Fig. 3), thereby sorting out all diatomic molecules, and tried to evaluate the properties of unknown molecules by interpolation.

Fig. 5: Table of N. Morozov’s radicals [8].
Physicist A. Boldyrev, on the contrary, calculated in advance the properties of all diatomic molecules (from s-, p-, and d-atoms) and brought the results to a table, marking the properties with color. (In Fig. 4 the systems with unpaired electrons are highlighted in color for the first 120 molecules.) As can be seen, it is very difficult to unambiguously associate the type of electron shell with the position of the molecule in the table.

From atoms to functional groups

In organic chemistry, since the time of Gerard’s “theory of types”, the properties of a complex molecule are traditionally reduced not so much to atoms as to certain aggregates of atoms – to functional groups that determine the “chemical face” of a molecule (hydroxyl, carbonyl, amino group). In this regard, the attempts of chemists to create classification tables (and even the PS’s) of the “types” themselves or functional groups are not surprising. In the 1890s N. Morozov (1854–1946). Arranged homologous series of hydrocarbon radicals in the form of a table [8] and found its amazing similarity with PS of elements (Fig. 5). For instance, methyl was considered analogous to fluorine, ethyl – analogous to chlorine etc.

From this parallel, he deduced the existence of the then-unknown group of “non-valence” elements. Such a group – noble gases – was soon really discovered by W. Ramzay, who, alas, did not know anything about the work of Morozov. (That time Morozov was a prisoner of the Shlisselburg fortress.)

A century later, in the 1980s, the German chemist A. Haas noted [9] that small monovalent radicals surrounded by fluorine atoms (like OF, NF, CF, SCF, N(CF), C(CF), etc.) are very similar in properties to halogens (therefore he called them “para-halogens”), divalent groups resemble oxygen or sulfur (therefore the name “para-chalcogens”), etc. Based on this analogy, Haas constructed the PS of fluorine-containing functional groups (called “para-elements” by him) that resembles the PS of elements (Fig. 6). With its help, he predicted a number of properties of new para-elements and experimentally obtained interesting and previously unknown subclasses of perfluorinated compounds.

![Fig. 6: “Para-elements” by A. Haas [9].](image_url)
From atoms to complex molecules

Despite the fact that an infinite number of molecules can be built from a finite number of atoms, chemists do not stop trying to search for molecular classifications and construct PS for molecules of varying degrees of complexity. Two such attempts are shown in Fig. 7, the PS of molecules by Shemyakin (a, b) and by Gorsky (c, d).

Shemyakin introduced the concept of “molecular number” [10–12], simply adding up the atomic numbers of the atoms that make up the molecule, and tried to make a thorough comparison and prediction of the properties of substances (as in Fig. 7a). The complexity of such a systematics is obvious: there are a lot of substances with the same molecular number (e.g. CO and NN have the same molecular number), so instead of a
table there is a complex space with cells (as in Fig. 7b). Gorsky [13] used even more complex redox indices for similar tables (Fig. 7c) and for comparing the properties of substances (Fig. 7d).

For some complex classes of organic substances, there are special rules that relate the stability of a molecule to the number of electrons (peculiar magic numbers), for example, the Hückel rule (for flat conjugated cycles) and its analogues for three-dimensional polyhedra (boron hydrides, metal clusters, etc.), Fig. 8. As was shown by the present author [14, 15], such rules can be combined by relating them to the topology of the molecular surface (namely, its Euler characteristic).

Touching upon the author’s early works in the field of natural classifications of molecules [1, 14–17] (known in the foreign literature as the “Babaev Hyper-periodic Table” [18]), we restrict ourselves to only the most important concepts. The main idea of our approach was to initially avoid multidimensionality in the construction of the PS for molecules. To this end, it was proposed to construct such two-dimensional tables, where ensembles of obviously similar (in structure and/or electronic properties) molecules are located in each cell. In one of the options (Fig. 9a), isovalent and isostructural isostere molecules (CO$_2$–N$_2$O, benzene-borazine, etc.) were placed in the same cells of the table. Although the “cell capacity” (the number of isosteres)
rapidly increases with the number of electrons (Fig. 9b), characteristic dual poles (organic-inorganic, acid-base, oxidizing-reducing agent, etc.) clearly appeared in such a flat table reminiscent of the dualism “metal-non-metal” in the PS of elements.

The main property of the obtained system was the appearance in it of a new type of molecular periodicity (“hyper-periodicity”), which does not follow from the PS of atoms. With an increase in the number of valence electrons for any N-atomic molecule through strictly defined intervals, the maximum possible (for a given N) topological “saturation” of the skeleton is achieved. Then, the type of molecular polyhedron is either preserved due to loss of connectivity (decay into a covalently disconnected associate), or connectivity is preserved due to a change in the polyhedron (often with a multicenter bond), Fig. 10a. As a result, the PS of molecules can be redrawn (Fig. 10b) in the form of horizontal “hyper periods” (with an equal number of non-hydrogen atoms) and vertical “hyper groups” (similarity either in the type polyhedron or in the connectivity

![Fig. 9:](image)

(a) PS of isostere ensembles of molecules [1, 16, 17] and typification at two poles. (b) Theoretically possible number of isostere ensembles in cells.

![Fig. 10:](image)

(a) With an increase in the number of electrons (from left to right), the type of polyhedron and the connection of the skeleton naturally change. (b) One of the projections of the hyper-periodic system of molecules: vertical hyper-groups and horizontal hyper-periods.
of molecular ensemble). It is curious that this simple idea combines the PS of hydrocarbons (by Morozov) and the PS of para-elements (Haas): both of them are only important (but by particular) types of hyper groups of a single PS of molecules.

Among the fundamentally different approaches one should be mention the work of D. Dias on the construction of the PS of an important subclass of substances – benzenoid hydrocarbons [19]. In this methodology,
the central place is occupied by the symmetry of molecules and the regular repeatability of symmetry elements upon transition to increasingly complex hydrocarbons, Fig. 11.

**PS in biology**

The natural classification of living organisms is one of the most intriguing problems of theoretical biology. Perhaps one of the first to realize it was V.N. Beklemishev (1890–1962); according to him: “The natural system of organisms, the construction of which is the ultimate goal of comparative morphology, is a law according to which a variety of organic forms is realized.”

The most in-depth analysis of the problem of building the natural systems belongs to A.A. Lyubishchev (whose name is known according to the story of D. Granin [20]). Trying to understand what principles of systematics in biology should be based on, Lyubishchev formulated the definition of a natural system (and its forms) as follows [21]: “The most perfect system is the one where all the features of an object are determined by its position in the system. The closer the system stands to this ideal, the less artificial it is, and a natural system should be called the one where the number of properties of the object put into a functional relationship with its position in the system is maximum. … Three forms of the natural system seem to be possible, which I will call hierarchical, combinative, and correlative. … In the latter, one attribute (or few) assumes a dominant value; everyone else is correlated with him.” According to Lyubishchev the

**Fig. 13**: The law of homologous series of plants by Vavilov.
The idea of constructing various types of PS in biology has a long history. Several years ago, a review by I.Yu. Popov [22] dedicated to the analysis of such attempts appeared. Although the author’s conclusion is pessimistic, he nevertheless noted a number of successful attempts to construct natural PS of individual families of biological objects (bacteria [Zavarzin], fungi [Vasiliev], pantopods [Shimkevich], etc.). One of the main problems in this area, apparently, is that the choice of the dominant attribute (with which others would have been “in a correlative relationship”) is not obvious. In one of Popov’s works [23], this is clearly illustrated by a diagram for an imaginary mammal (Fig. 12), where completely randomly selected characters (say, the length of the tail and ears) may well serve as the basis for a peculiar PS.

Does this mean that all attempts to search for and construct PS in biology are doomed? In our opinion, the most promising are those approaches in which the system-wide characteristics of complex objects that reflect the composition, structure and symmetry of their parts come to the fore. Note that these very concepts are the clearest definitions in chemical taxonomy and crystallography. There are examples in biology when the accentuation of these very characteristics led to very striking results. So is the law of homologous series of plants by N.I. Vavilov (1887–1943), Fig. 13. Here the principle of homology, well developed in chemistry and taken as a system-wide, led to useful results.

Other examples of unexpected classifications in botany are presented in the works of Yu.A. Urmantsev [24–27]. The main emphasis was placed on the principle of bio-isomerism, generalizing the phenomenon of chemical isomerism. It turned out that the structure of the arrangement of the petals in the flower cups (Fig. 14a) or the veins on the leaves (Fig. 14b) has a clear parallel with the number of optical and geometric isomers of the molecules with the same number of parts (only the way the parts are arranged in space is important).

In the same context, it is worth mentioning the recent book by V. Pavlov [28], devoted to the PS of arthropods (ARTHROPODA). The prognostic nature of this PS is quite convincing: for example, one can predict...
the properties of a certain organism (say, a long-extinct trilobite), and then try to find traces of its existence experimentally (Fig. 15).

This very incomplete review shows the influence that the principle of periodicity has on the development of natural science for 150 years after its discovery. The riddle and harmony of the periodic system does not cease to excite scientists of various fields of science.

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Author’s web resource on the topic of molecular periodicity: http://www.chem.msu.ru/eng/misc/babaev/match/.

Fig. 15: Pavlov’s PS of arthropods and prediction of concrete structure of a trilobite.

References


