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D — Mathematics and the Periodic Table
Some Mathematical Aspects
of the Periodic Table

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D — Mathematics and the Periodic Table

Some Mathematical Aspects of the Periodic Table

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Although until now mathematicians have little to say on the Periodic Table, we could not fully understand its structure without Mathematics. On the other hand, Mathematical Chemistry is an expanding interdisciplinary area and recent works have shown the importance of the underlying mathematics of the periodic table in diverse areas such as group theory, topology, information theory and, of course, quantum mechanics. As an introduction to the Lisbon 2019 mathematics journey at the Academy of Sciences of Lisbon, celebrating the “*International Year of the Periodic Table of Chemical Elements*”, these notes intend to present a short synthesis to some aspects related to the periodic table, from the perspective of a mathematician.

PERSPECTIVES ON THE 150TH YEAR OF THE PERIODIC TABLE

Since ancient times the search of the composition of matter led the Greek philosophers to sustain the existence of four elements: air (hot and wet), fire (hot and dry), earth (cold and dry) and water (cold and wet). Aristotle (384-322 BCE) added a fifth element, the ether, and Kepler in his *Harmonice Mundi* (1619) associated them with the five platonic solids (fire – tetrahedron, air – octahedron, earth – cube, water – icosahedron and ether – dodecahedron), which were mathematically described in the Book XIII of the *Elements* (~300 BCE) of Euclid. Published in 1789, Lavoisier’s list with 33 elements or “simple substances” that could be isolated from compounds and not decomposed further was a step towards the organization by chemists from simple substances to abstract elements. The discovery of periodicity in the chemical elements and its representation in tables in the 1860’s has been considered “an excellent example of a simultaneous discovery” “by at least six authors in over a period of 7 years” [S1]. The five Mendeleev’s predecessors were: the French geologist E. B. de Chancourtois with a three dimensional periodicity arranged in a suitable way on a spiral displaying of the elements with similar properties in order of atomic weight around a cylinder, in 1862; the English chemists J. Newlands, who in 1863 classified the elements into a total of seven groups and explored relationships among their atomic weights, and W. Odling, who published in 1864 a periodic table with 57 elements; the Danish scientist G.

¹ (CMAFeIO/Ciências/ULisboa)

Hinrichs, who in 1867 proposed a plane spiral representation of the periodic system, and the German chemist L. Meyer, who published his first periodic table with 28 elements in 1862, enlarged to 50 elements in 1864 and to a more elaborated one in 1868

In 1869, the Russian chemist Dmitri Mendeleev (1834-1907) published his first table with 66 entries based on the only 61 elements known at that time, but it had a strong prediction potential to accommodate new elements, including the Gallium (1875), the Scandium (1879) and the Germanium (1886). After several revisions and corrections, by 1890 his table had been universally recognised as a piece of basis of chemical knowledge [S2], becoming one of the indispensable tools for science and an icon for scientific inquiry. With about a thousand of versions during one and half century [S2], the current Periodic Table reached 118 elements with the synthesis in 2002 of the Oganesson, ${}_{118}\text{Og}$, although only 94 occur naturally.

In 2019 the European Chemical Society released a new kind of Periodic Table with *the 90 natural elements that make up everything*. This colourful table, showing an impressive visualisation of those elements, is based in the proportion between the area occupied by each element and its approximate amount existing in the earth's crust and atmosphere, in particular referring the elements that are used in a smartphone. It was recently been updated to highlight the unique position of carbon (C) and to

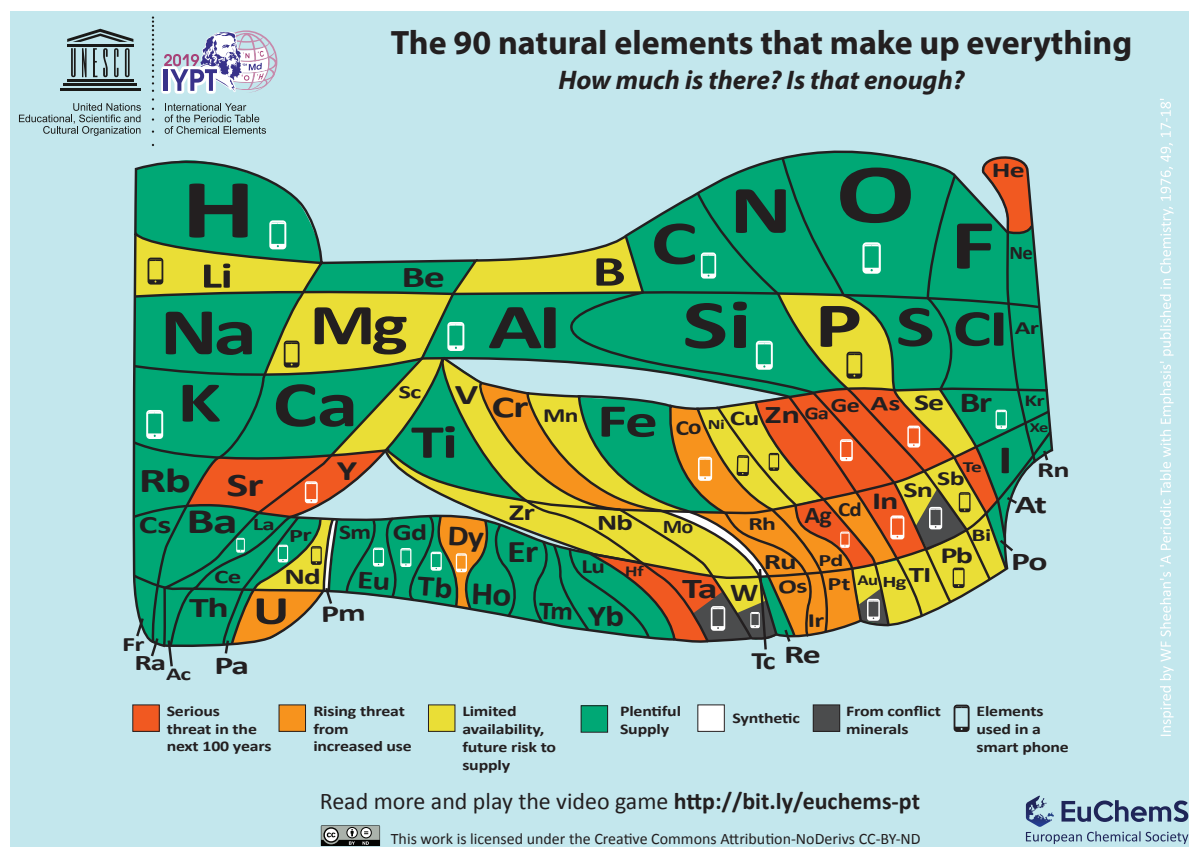


Figure 1

The Element Scarcity – EuChemS Periodic Table <https://www.euchems.eu/euchems-periodic-table/>

introduce the concept of sustainability adding in the subtitle to the questions *How much is there?* and *Is that enough?* a third question *Is it sustainable?*

All around the world a large number of publications, conferences, symposia and other activities were organized by chemical societies, schools, museums, universities, etc. while an opening ceremony took place at the UNESCO headquarters in Paris in January 2019. In particular, philatelic celebrations of the IYPT2019 took place in many countries and in Portugal two stamps were released on 24 July 2019: one with the four classical elements from Ancient Greece and the symbol of the first element of the table and the most common of the Universe, the hydrogen; the other with a portrait of Mendeleev and the chemical symbol Md of the mendeleevium, its atomic number $Z = 101$ and its atomic mass $A = 258$.

Another perspective from the mathematician and musician Tom Lehrer, who also lectured mathematics and music theater at the University of California, Santa Cruz, is the song "*The Elements*", in which he set names of the chemical elements to the tune of a music by Gilbert and Sullivan and can be seen in a live performance registered in Copenhagen in 1967 [L].



Figure 2
The two stamps issued by the *Correios* of Portugal celebrating the *International Year of the Periodic Table*.

PERIODIC TABLE, QUANTUM THEORY AND MATHEMATICS

In the turn of the twentieth century, the development of atomic physics had a profound influence on chemistry and, in particular, in the explanation and the development of the periodic table. The discovery of the atomic number (Z) in the 1910's, by Antonius van den Broek, a Dutch amateur physicist, who first realized that the number of an element in the periodic table corresponds to the charge of its atomic nucleus, was followed the fundamental contribution of the English Henry Moseley (1887-1915), who verified that when representing the square root of the radiation frequency as a function of the order number in the periodic system, a straight line was obtained, a reflection of some property of the atomic structure. This property is described by an affine equation relating the square root of the frequency and the atomic number or number of positive charges of the nucleus and it was "the first time a mathematical equation provided a way to ordered the elements as a function of a very simple variable as it was the atomic number"[MY] and chemists "had an unambiguous method for determining exactly how many elements were present and where in the periodic system any gaps might still remain to be occupied by new elements" [S2].

As observed by Manuel Yáñez at the Lisbon meeting, the following quotation of the Belgian scientist Adolph Quetelet (1796-1874) is most appropriate: “The more the physical sciences progress, the more they tend to enter the domain of mathematics, which is like a center towards which everything converges. We can judge the degree of perfection achieved by a science by the ease with which it can be subjected to calculation”.

A first clear and deep explanation of the periodic table coming from new mathematics methods of Quantum Mechanics in 1925, after Schrödinger solved the one dimensional partial derivatives equation that now has his name and was able to accurately describe the electronic properties and the spectra of hydrogen-like systems. This breakthrough pioneered the way calculating the properties of atoms by means of approximated methods, like the Hartree-Fock model and the Thomas-Fermi method leading to density functional theories.

The initial success of Quantum Mechanics to understand the hydrogen atom raised the natural question of studying the larger atoms and led to the famous and controversial statement by the English theoretical physicist Paul Dirac in 1929: “The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble”. However, if the physical programme of reduction of chemistry has been highly successful and “has literally re-presented the periodic system and has provided it with a theoretical justification”, it “turned out to be only partly fulfilled”, as for example, “the lengths of successive periods have not yet been strictly deduced from the theory” [S2].

Numerous other problems were encountered and the interaction between Quantum Mechanics and Mathematics in the twentieth century was enormous. It has generated relevant mathematical research not only for simplified quantum atomic models, starting with the equation

$$H \Psi = \lambda \Psi$$

relating the Hamiltonian H applied to the wave function Ψ and the eigenvalue λ associated with the quantic number, which contributed to the theory of Hilbert spaces, but also to other mathematical disciplines, namely, semi classical asymptotics, field theories, potential theory, computational issues and analytic number theory.

To illustrate two significant episodes of the influence of Quantum Mechanics into Functional Analysis and Operator Theory, we quote first the American mathematician Marshall Stone, who in 1970 wrote: “Stimulated by an interest in quantum mechanics, John von Neumann (1903-1957) began the work in operator theory... The result was a paper von Neumann submitted for publication to the *Mathematische Zeitschrift* but later withdrew. The reason for this withdrawal was that in 1928 Ehrard Schimidt and myself, independently, saw the role which could be played in the theory by the concept of the adjoint operator, and the importance which should be attached to *self-adjoint operators*. When von Neumann learned from Professor Schmidt of this observation, he was able to rewrite his paper in a more satisfactory and complete form... Incidentally, for permission to withdraw the paper, the publisher exacted from Professor von Neumann a promise to write a book on quantum mechanics. The book soon appeared and has become one of the classics of modern physics (*Foundations of Quantum Mechanics*, Springer-Verlag, 1932)”.

A second and more direct and specific statement of 1951, by the Japanese mathematician Tosio Kato (1917-1999), is also very significant: “The fundamental quality required of operators representing physical quantities in quantum mechanics is that they be *hypermaximal* or *self-adjoint* in the strict sense employed in the theory of Hilbert space, which is equivalent to saying that the eigenvalue problem is completely solvable for them, that is, *there exists a complete set (discrete or continuous) of eigenfunctions*. (...) The main purpose of the present paper is to show that the Schrödinger Hamiltonian operator of every atom, molecule, or ion, in short, of every system composed of a finite number of particles interacting with each other through a potential energy, for instance of Coulomb type, is *essentially self-adjoint*. Thus, our result serves as a mathematical basis for all theoretical works concerning nonrelativistic quantum mechanics, for they always presuppose, at least tacitly, the self-adjointness of Hamiltonian operators.” [K].

In the last decade of the twentieth century, the American mathematician Charles Fefferman (born in 1949, received the Fields Medal in 1978) has considered, with L. Seco and A. Córdoba, a mathematical problem arising from quantum mechanics which relates atoms and analytic number theory [F]. This problem is reminiscent to a question appearing in Number Theory for counting Lattice Points inside circles and spheres, which was solved for a disc of radius R , by the English mathematician Hardy in 1913, who showed that number to be of the order $\pi R^2 + O(R^{2/3})$. That mathematical-physics problem is to compute the ground-state energy $E(Z)$ of a single atom with large atomic number Z . Although not a very accuracy determination of the ground state energies for larger atoms can be achieved today, there are nevertheless some interesting asymptotic approximation results in terms of fractional expansions of the number Z . As it is explained in [C], $E(Z)$ being represented by the standard Schrödinger Hamiltonian with Coulomb potentials, and the semiclassical approximation, has the rigorous expansion

$$E(Z) = C_{TF} Z^{7/3} + C_S Z^2 + C_{SD} Z^{5/3} + \Psi_Q(Z) + \dots,$$

which last term is oscillatory and behaves like $|\Psi_Q(Z)| \leq c_1 Z^{3/2}$, where c_1 is a universal constant, and has the average of $|\Psi_Q| \sim Z^{3/2}$.

The mathematical formalism of quantum mechanics and the need of approximating solutions created a gap with the traditional chemical view, which is being bridged by the powerful methods of computational and quantum chemistry. Considering molecules as “Many-Body” systems with N nuclei and n electrons, under the Born-Oppenheimer approximation nuclei are mere artifacts to provide the external potential that holds and shapes the electronic cloud. The shape of the wave function resulting from the overlap of so many different basis functions has no resemblance with the original atoms that made the molecule. Adelino Galvão observed in [G] that the topological analysis of the charge density provides a tool in which the atoms remain the building blocks of all the matter that exists fitting its molecular function.

THE MATHEMATICS OF THE PERIODIC TABLE

This is the title of a recent collective book [RK], published in 2006 and composed of 12 chapters by theoretical chemists, theoretical physicists and applied mathematicians. It is the first collective book focused solely on the mathematical aspects of the Periodic Table. The authors describe some

mathematical methods that they have been applied in their work. Although a collection of articles with eclectic material, this book presents an interesting range of ideas, concepts and suggests different approaches and perspectives to the study of the Periodic Table.

The first chapter, written by D. H. Rouvray, one of the editors, raises the interesting question of “the ultimate size of the periodic table”, after displaying a list of all the chemical elements discovered since the 17th century, when Phosphorus was first isolated, followed by the 19, the 51 and the 33 elements isolated, respectively, in the 18th, the 19th and the 20th century. The history of the prediction about the upper limit of the periodic table have had several variations with the discovery of the superheavy elements, and nowadays the highest is the Oganesson, the 118th element. It remains a conceivable possibility that the development of new technologies will enlarge this number. In fact, a concrete proposal of a periodic table up to atomic number $Z \leq 172$ can be found in [P], which was based on computational methods developing further the Dirac-Fock calculations done earlier in the 1970's, in order to predict the electron configurations of the elements from $Z = 119$ up to $Z = 172$, being this number a possible limit for stable electron shells within the quantum electrodynamic theory.

Among the other chapters of [RK], the fifth one is on a topological study of the periodic system by G. Restrepo, H. Mesa, J. L. Villaveces and E. J. Llanos. Defining appropriate topologies on the set of chemical elements based on similarity trees and introducing a space of physicochemical properties, the authors claim to have shown a robust way of classifying the elements into metals, meta-metals, semimetals and non-metals. They also concluded the existence of “an underlying topological structure to the set of chemical elements that is responsible for the well-known periodic properties of the elements as well as for some other properties not usually associated with the Periodic Law.”

The eighth chapter, by D. Bonchev, is an information-theoretical analysis on the periodicity of the chemical elements and nuclides. Based on the Shannon's information theory applied to finite discrete sets, this chapter describes a number of information indices for characterizing the electronic and nuclear structure of atoms of the chemical elements, which similarity in their periodic trends were used by the author to predict the binding energies of 45 unsynthesized isotopes of the elements from $Z = 101$ until $Z = 118$, most of them confirmed with a high accuracy. Bonchev claims that the chosen “descriptors of atomic structure express in different ways the information content of the atom encoded in the distributions of the atomic particles, namely electrons, protons and neutrons.”

Finally, the last three chapters of [RK], namely “*Group Theory of the Periodic Table*”, by O. Novaro, “*A Group-Theoretical Approach to the Periodic Table: Old and New Developments*”, by M. R. Kibler, and “*Group Theory Applied to the Periodic Table of the Elements*”, by V. N. Ostrovsky, make almost a third of the book. The relevance of the applications of Group Theory to the Periodic Table is well known since the works of V.A. Fock and V. Bargman in the 1930's demonstrated that the $O(4)$ symmetry of the hydrogen atom stems from the conservation of two constants of motion.

Nowadays all group-theoretical approaches to the Periodic Table are based on the fact that the problems of classification within Quantum Mechanics are closed related to symmetry questions that can be treated using Group Theory. One of them, the Elementary Particle Approach, according to the theoretical physicist V.N. Ostrovsky, “claims to treat an element as a whole, as some non-split entity.

In particular, a dynamic group of the Periodic Table implements a dream of the alchemists, namely transmutation of elements. A mere application of the dynamic group generators transforms one chemical element into another, thus implementing the ambitious goal. The remaining problem is that the chemical elements are defined as vectors in some abstract Hilbert space, and nobody knows how to connect this with physicochemical reality.” [RK, page 305].

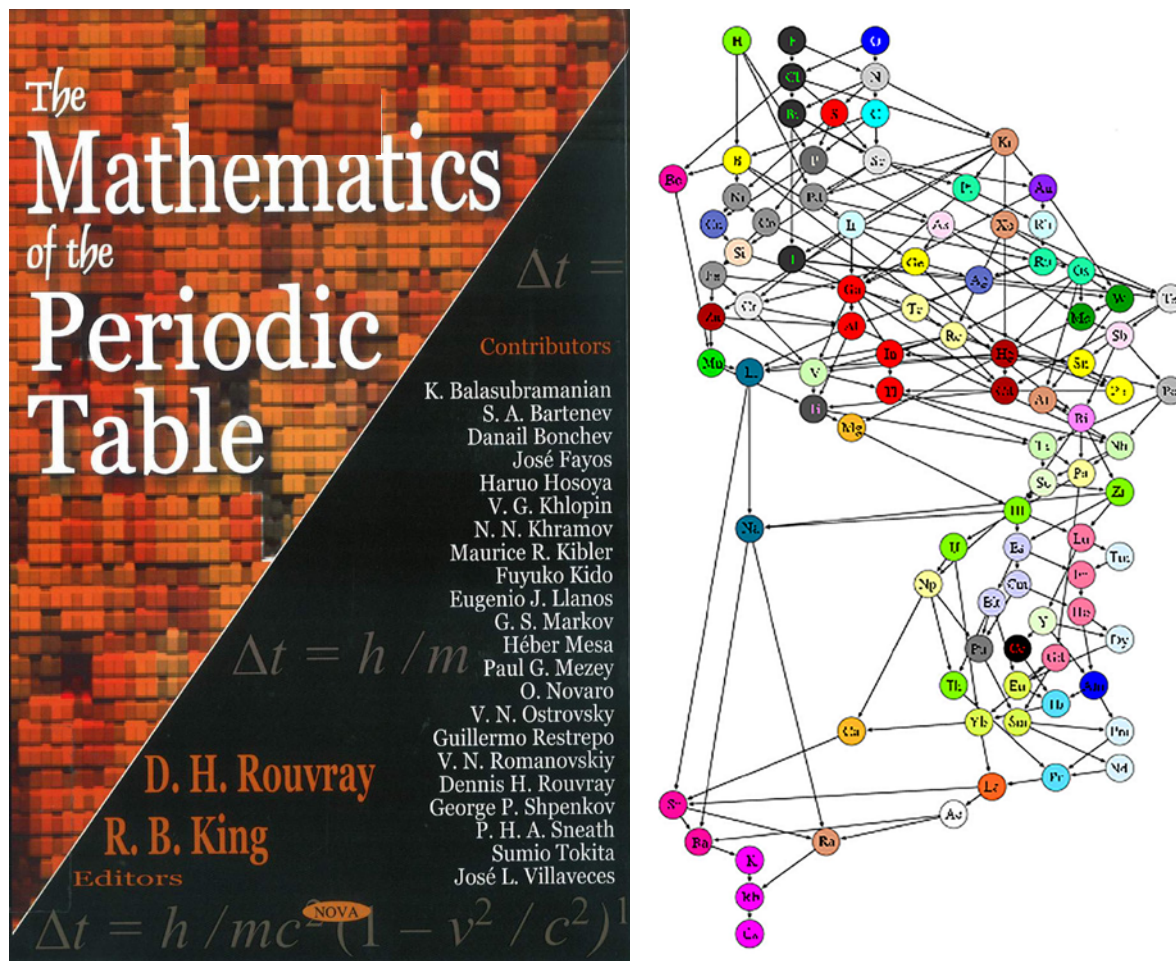


Figure 3
The cover of the book [RK] (left) and the coloured hypergraph of the elements by [LR] (right)

A comprehensive exposition of a mathematical approach to the classification of chemical elements based on group theory and principles of quantum mechanics can be found in the 2016 book [Fet], by the Russian mathematician A. I. Fet (1924-2007), which is a translation from the 2010 Russian edition and was written in 1984. Starting with the Coulomb potential and the hydrogen atom as an illustration of the application of group theory to quantum mechanics and chemistry, after the tutorial chapters on the mathematical structures and quantum field theory, the book treats the symmetry group of chemical elements and the comparison with experimental data and a classification of chemical elements. A more recent introduction to the applications of special groups and a comprehensive

overview of symmetries in physics and chemistry, including the Periodic Table, can be found in the book [TC].

Recently, in another interesting mathematical description of the Periodic System based on the relations of order and similarity of chemical elements, it is proposed in [LR] an ordered hypergraph (see figure 3), where the hyperedges are similarity classes to describe the structure of the Periodic Table. We recall that a graph is a set of objects (vertices) in which some pairs are related in some sense, by an edge. A hypergraph is a generalisation of a graph, in which an edge can join any number of vertices and not necessarily only two.

After clarifying the difference between *periodic system* of chemical elements, as being the structure resulting from considering the order and similarity of chemical elements, from a *periodic table*, which is a mapping of the periodic system into another space, normally bi-dimensional, Leal and Restrepo in [LR] define the Mendeleevian periodic system as an ordered partition composed by the set of chemical elements, the order relation by the atomic number and a classification by some properties of the elements. They proceed with a formalization and generalization of “the periodic system as a set endowed with a system of similarity classes, whose elements hold an order relation”, which “structure corresponds to an ordered hypergraph, where similarity classes are hyperedges”.

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