A Mathematical Celebration of the 150th Anniversary of the Periodic Table

by **José Francisco Rodrigues***

In a joint initiative of the *Centro Internacional de Matemática* (CIM) and the *Instituto de Ciencias Matemáticas* (ICMAT) a simbolic mathematical celebration of the Periodic Table took place at the Academy of Sciences of Lisbon, the 21st November 2019. It consisted of four talks, by two mathematicians and two chemists: *Some mathematical aspects of the periodic table*, by José Francisco Rodrigues (CIM and FCiências/ULisboa), *The power of systematisation. The importance of precision*, by Manuel Yáñez and Otilia Mo (Universidad Autónoma de Madrid), *The periodic table: Are atoms the bricks of molecules?* by Adelino Galvão (ISTécnico/ULisboa) and *Counting lattice points and atomic energies oscillations*, by Antonio Córdoba (ICMAT and UAMadrid). They were streamed online and their record can be found at http://www.cim.pt/agenda/event/208.

The UNESCO decided to celebrate the year 2019 as the "*International Year of the Periodic Table of Chemical Elements*" — https://iypt2019.org/ — commemorating all around the world the 150th anniversary since Dmitry Mendeleev discovered the Periodic System only with 61 elements, but containing a strong prediction potential to accommodate new elements reaching nowadays 118. The Periodic Table is of central importance to chemistry and after one and half century of life it became one of the indispensable tools for science and an icon for scientific inquiry. Although until now mathematicians have little to say on the periodic table, the mathematical chemistry is an expanding interdisciplinary area. 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. The introductory talk of the Lisbon meeting in-

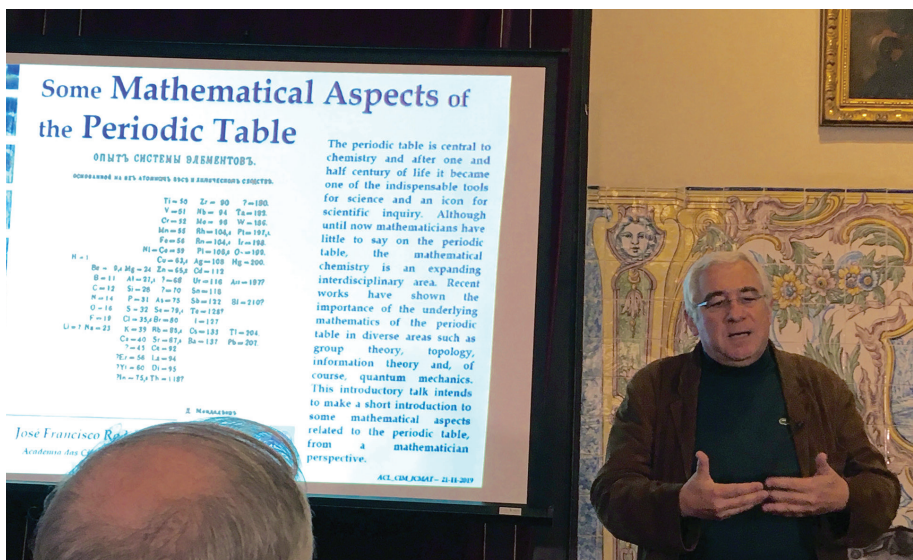* CMAFcIO, Faculdade de Ciências, Universidade de Lisboa

Figure 1.—The Periodic Table of Mendeleev shown in the talk by J. F. Rodrigues.

tended to make a short introduction to some mathematical aspects related to the periodic table, from the perspective of a mathematician.

After referring that the initial idea of this mathematical meeting was originated by the reading of the article on *Matemáticas alrededor de la tabla periódica*, by Antonio Córdoba, published the 4th January 2019 in the section *Café y Teoremas* in the Spanish newspaper *El País*, and decided together at the ERCOM meeting held in March in Cambridge by the directors of CIM and ICMAT, Rodrigues has started his presentation by evoking the role of Mathematics in Quantum Mechanics, and vice versa, by displaying the equation

$$H\Psi = E\Psi$$

relating the Hamiltonian H applied to the wave function Ψ and the eigenvalue E associated with the quantic number, and referring the classical work of John von Neumann (1903–1957) on the *Foundations of Quantum Mechanics* (1932). He quoted a significant statement of 1951 by Tosio Kato: *The fundamental quality required of operators representing physical quantities in quantum mechanics is that hey 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 nonrelativitic quantum mechanics* [K].

Some chapters of the recent collective book *The Mathematics of the Periodic Table* [RK], which contains eclectic material on some mathematical methods and a range of ideas, concepts and different approaches applied to the study of the Periodic Table, were commented on the first talk. The first chapter, written by 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 (Og), the 118th element. It remains a conceivable possibility that the development of new technologies will enlarge this number.

Among the other chapters of [RK], the one on a topological study of the periodic system, by defining topologies on the set of chemical elements based on similarity trees and introducing a space of physicochemical properties, has shown a robust way of classifying the elements into metals, metametals, semimetals and non-metals. Based on the Shannon's information theory applied to finite discrete sets, another chapter described a number of information indices for characterizing the electronic and nuclear structure of atoms of the chemical elements, which similarity in
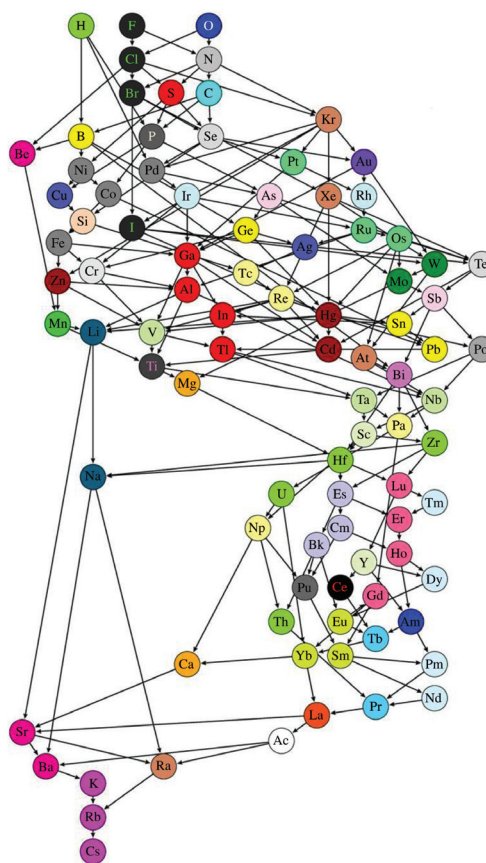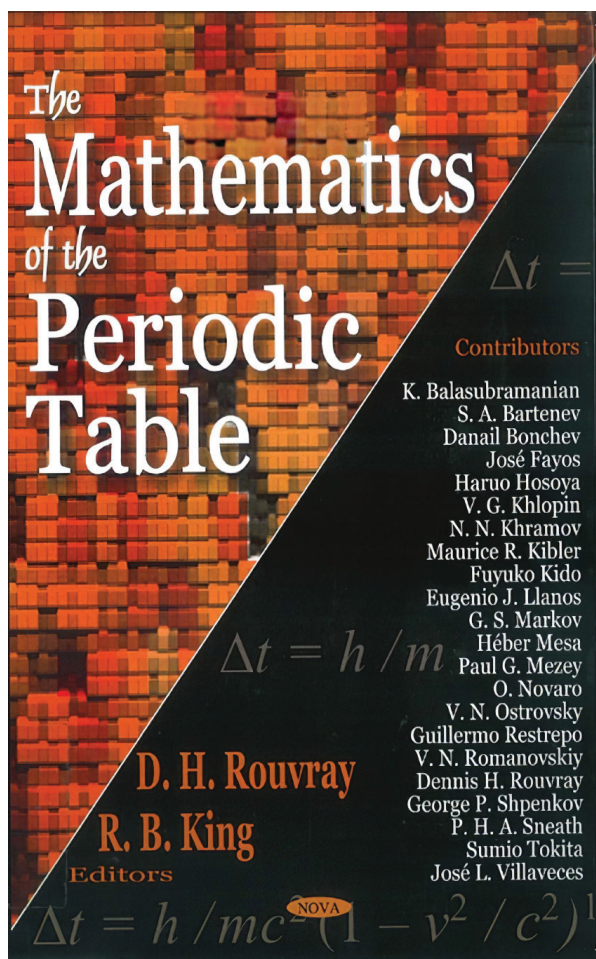
Figure 2.—The cover page of [RK] and the hypergraph of W. Leal and G. Restrepo from [LR].

their periodic trends were used by D. Bonchev to predict the binding energies of 45 unsynthesized isotopes of the elements 101 to 118. Most of them were confirmed with a high accuracy. Finally, three chapters of [RK], almost a third of the book, describe the applications of Group Theory to the Periodic Table. Its relevance 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 there are several group-theoretical approaches to the Periodic Table, but all of them 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 and 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].

Recently, in another interesting mathematical description of the Periodic System based on the relations of order and similarity of chemical elements, in [LR] it is proposed an ordered hypergraph (see figure 2), where the hyperedges are similarity classes to describe the structure of the Periodic Table, which has been at the core of chemistry for more than 150 years.

The first talk ended with a completely different view on the Periodic Table by the mathematician and musician Tom Lehrer, who lectured mathematics and music theater at the University of Califormia, Santa Cruz, and sang "*The Elements*" [L], in which he set names of the chemical elements to the tune of a music by Gilbert and Sullivan.

Manuel Yáñez started his presentation on the power of systematisation and the importance of precision, stating clearly that the revolution of Mendeleev Table was, one

Figure 3—The contemporary Periodic Table and the presentation of Manuel Yáñez.

hundred and fifty years ago, "*the first important systematization in the realm of chemistry was done, ordering the elements in terms of its atomic mass. This first attempt was crucial even though not totally correct. A better knowledge of the atomic structure improved this initial systematization in terms of the atomic number; but a real understanding of the periodicity in the atomic properties was possible only when the mathematical functions describing the electrons within an atom were obtained*" [MY]. In fact, the initial criterion (atomic mass) was pure empiricism but the elements appeared grouped in families with common chemical properties, a question that had no answer at that moment. In the words of Niels Bohr: The Periodic Table was the guiding star for the exploration of the fields of chemistry and physics. But the ordering was not completely satisfactory. For instance, tellurium-iodine, argon-potassium and cobalt-nickel couples should be located in the reversed order. But some predictions were totally correct: for instance, when isolated and characterised, Eka-Boron was renamed Scandium (Sc), Eka-Aluminum turned into Gallium (Ga), Eka-Manganesse into Technetium (Tc), and Eka-silicon into Germanium (Ge). The final version of the table was achieved thanks to the periodic law presented by the British Henry Moseley at the beginning of the 20th century. Moseley 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 (Z) or number of positive charges of the nucleus. But still it was not evident which were the real reasons for this periodicity!

With an interesting quotation of the Belgian scientist A. Quetelet (1796-1874), "*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*", Manuel Yáñez observed that the first clear explanation came from Mathematics starting with quantization in 1925, with $H\Psi = E\Psi$, after Schrödinger established and solved the partial derivatives equation that now has his name and was able to accurately describe the electronic properties and the spectra of hydrogen-like systems. But there is always a but — this equation cannot be easily solved for more than 1 electron, raising difficult questions of efficient approximations and, despite many impressive progresses, even today the placement of the elements has not settled after 150 years, starting from the very first element. Nevertheless, the use of the variational principle looking for the minimal energy of an atomic and molecular system was the engine behind this understanding, though soon it became also clear that, in some specific cases, second order properties could be not adequately described even if the precision got for the ener-

The 90 natural elements that make up everything
How much is there? Is that enough?
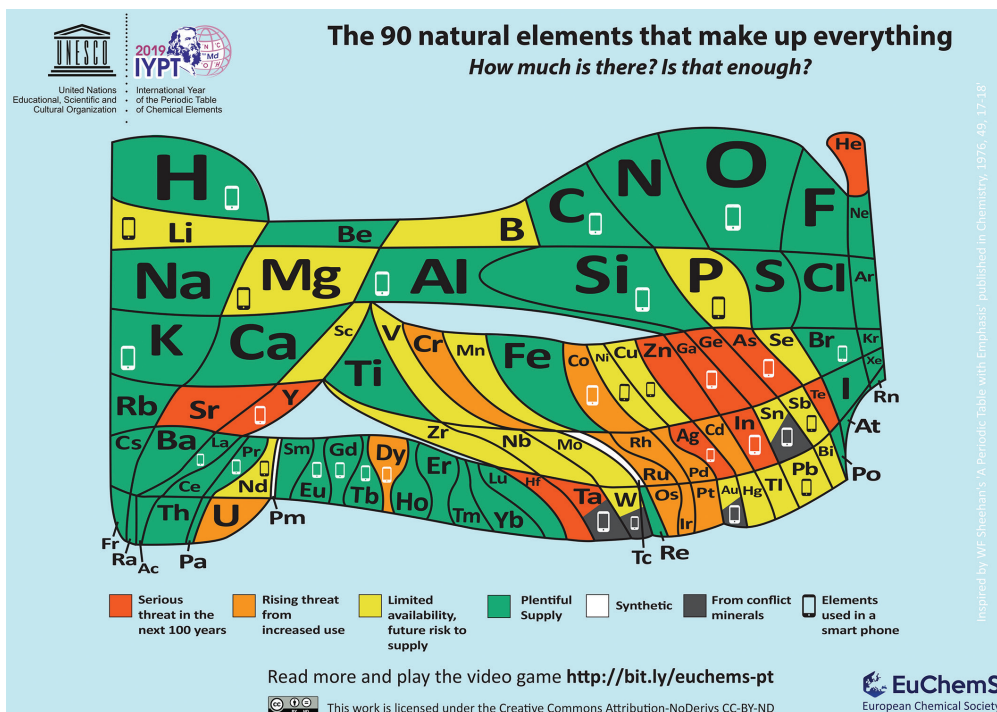
Figure 4—The visualisation of the 90 natural elements in this table is based in the proportion between the area occupied by each element and its approximate amount existing in the earth's crust and atmosphere.

gy was large. Magnetic properties are a good example, or the singularity of the elements of the first row of the periodic table with respect to the others within the same group. Then he presented recent results that show that the Periodic Table is still a living object with many surprises yet to be unravelled.

For example, after the inclusion in the theory of relativistic effects in the 1970's, Yáñez described the great difference between the nonrelativistic and the relativistic effects on the properties of gold. He concluded his presentation by showing the colourful table of the European Chemical Society showing an impressive visualisation of the 90 natural elements, that make everything, which 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.

Adelino Galvão proposed to answer the question he had formulated in the title of his talk — *Are atoms the bricks of molecules?* — from the chemists' point of view as architects of the electronic cloud to give it shape and function. 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. As explained in his talk, atomic nuclei are bare necessities (like rebars in concrete) to provide the external potential

that hold and shape electrons within the molecule, but otherwise useless in what concerns its chemical properties. Those are defined, in the Quantum formalism, by a statistical distribution function that it is believed to be expressed by a linear expansion in a basis of pre-existent atomic centered distribution functions. Time has proved that this approach must be completed with extra polarization and diffuse functions to get results within experimental accuracy.

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. For instance, in the C-O molecule how can one divide between C and O the charge density in the middle of the bond? Then, Galvão observed that the traditional chemical concepts like bonds, rings, nonbonding pairs, electrophilic, nucleophilic, electronegativity, functional group, etc. are lost in the wave function formalism. Those can be recovered by proving that the wave function uniquely defines the charge density (and vice-versa) and both are uniquely defined by the external potential. In his exposition, Galvão has shown, by topological analysis of the charge density, how to recover the traditional chemical language, such as atoms, in a quantum formalism and precisely define what is an atom in a molecule. Most chemical properties can be defined by the critical points in the charge density maps (zero gradient) and the corresponding eigenvalues of the hessian: 3 negative eigenvalues (maxima) are atomic posi-
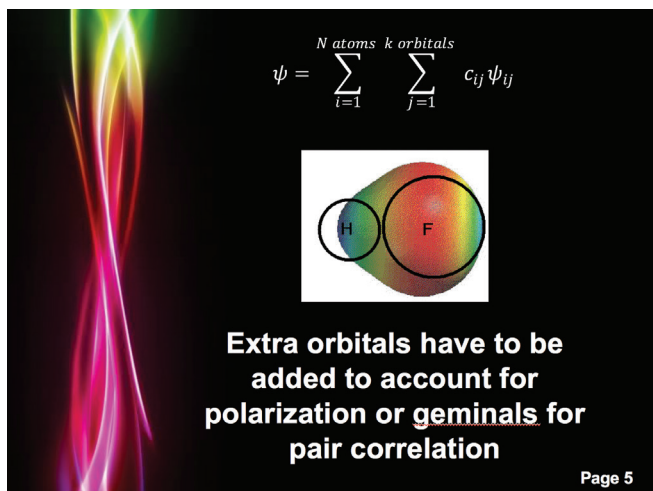
Figure 5.—Adelino Galvão explaining one of the slides of his presentation.

tions; two negative ones (saddle points) are bonds, and two positive ones are rings. The gradient relief maps provide dimension to atomic positions by means of its zero-flow surface under the Gauss theorem. Reactivity insight is given by the topology of the Laplacian whose signal maps areas of charge depletion (favourable to nucleophilic attacks) or charge concentration (susceptible to electrophilic attacks). As an example, the lone pairs of water are nothing more than a volume where the Laplacian is extremely negative. The eigenvectors of the hessian at these locations provide the orientation of the lone pairs. To finalize he has shown that moving from meaningless (in the physical sense) statistical distributions to charge densities reconciles classic and quantum chemistry and enables direct comparison with experimental quantities obtainable by diffraction techniques.

The initial success of Quantum Mechanics to understand the hydrogen atom raised the natural question of studying the larger atoms. Numerous problems were encountered and it has generated relevant mathematical research for simplified quantum atomic models, namely, semi classical asymptotics, field theories, potential theory, computational issues and analytic number theory. Successful developments were made in the framework of the Thomas-Fermi theory.

In his talk on *Counting lattice points and atomic energies os-*

cillations, Antonio Córdoba briefly reviewed one aspect of an ambitious plan to explain the periodic table from first principles of Quantum Mechanics, by reporting collaboration with Charles Fefferman (Princeton University) and Luis Seco (University of Toronto), in their joint work [CFT]. Although not a very accuracy determination of the ground state energies for larger atoms can be achieved today, there are nevertheless some interesting results that can be obtained involving almost periodic trigonometric sums which are reminiscent of those appearing in Number Theory for counting Lattice Points inside circles or spheres.

After introducing the ground state energy of a neutral atom $E(\mathscr{Z})$ with nuclear charge $\mathscr{Z}$, which is represented by the standard Schrödinger Hamiltonian with Coulomb potentials, and the semiclassical approximation, Córdoba described rigorous results for the expansion

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

The leading term on $\mathscr{Z}^{7/3}$ was conjectured by Thomas and Fermi in 1927 and proved rigorously by E. H. Lieb and B. Simon in 1977. The middle term in $\mathscr{Z}^2$ was explained in 1952 by J.M.C. Scott, through numerical computations, and proved in the works of K. H. Siedentop and R. Weikard in 1989 and W. Hughes in 1990. Finally, the second correction in $\mathscr{Z}^{5/3}$ was conjectured by P. Dirac in 1930 and proposed by J. Schinger in 1981, but was proved

Figure 6.—Antonio Córdoba describing the main result on the fourth term of the ground state energy of a neutral atom in terms of its nuclear charge.

in 1990–94 in a series of papers by C. Fefferman and L. Seco (see [C] for references). The question of higher order expansions is still under investigation, but Córdoba presented a theorem of [CFT] on the next term, which is oscillatory, by stating that $|\Psi_Q(\mathscr{Z})| \le c_1 \mathscr{Z}^{3/2}$, where c_1 is a universal constant, and the average of $|\Psi_Q| \sim \mathscr{Z}^{3/2}$. This problem is strictly related to the basic number-theoretic problem of estimating the number of lattice points inside a domain enclosed by a given curve. That theorem of Córdoba-Fefferman-Seco is a relevant estimate to the bound of the size $\mathscr{Z}^{\gamma}$ with $\gamma < 3/2$ for the Thomas-Fermi density.

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