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# The periodic table and the legacies of Évariste Galois and Sophus Lie

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*Abstract*

*The shell structure of matter is a unifying principle, from the fixed orbits of the planets, to the gyrating electrons in an atom, and the dance of the quarks in protons and neutrons. It puts Mendeleev's Periodic System, proposed 150 years ago, into the historical perspective of two other great taxonomies: the earlier planetary law of Titius-Bode, and the later quark hypothesis by Gell-Mann. In the case of the quarks, use was made of the theory of symmetry groups, which was created around 1830 in a flash of genius by* Évariste *Galois. Its subsequent application to the symmetry of continua is due to Sophus Lie. In this respect the classification of hadronic matter by group theory shows a more advanced and mature form of theory, as compared to the quantum mechanical treatment of the Periodic System. In 1969, at the centennial of Mendeleev's discovery, Löwdin noted how remarkable it was that the periodicity of the table had not been derived from first principles. This challenge is calling for a comprehensive theory of atomic shell structure. The present contribution relates the search of the deep symmetries at the origin of the table. This leads to an unexpected confrontation with the algebras of Sophus Lie.*

## 1. A portrait gallery

To bring order to chaos is one of the key elements of scientific discoveries. It starts by proposing a taxonomy. Such was the classification of the chemical elements in a periodic system by Mendeleev in 1869. The year 2019 was proclaimed as the international year of the periodic table to commemorate the 150$^{th}$ anniversary of this exceptional achievement. This is a welcome occasion to put Mendeleev's contribution in a broader perspective and compare it to similar classification rules in natural science [1]. In our portrait gallery of great 'rule seekers' (Figure 1) we place Mendeleev in the company of predecessors Titius and Bode, who discovered the law of the planetary distances approximately a century earlier, and of worthy successor Murray Gell-Mann, who came up with the classification of hadronic matter almost a century later. However, before the start of our guided tour, it is well to remind that while these individual scientists were credited with these discoveries, history shows little mercy to their contemporaries who often made equally valuable contributions.

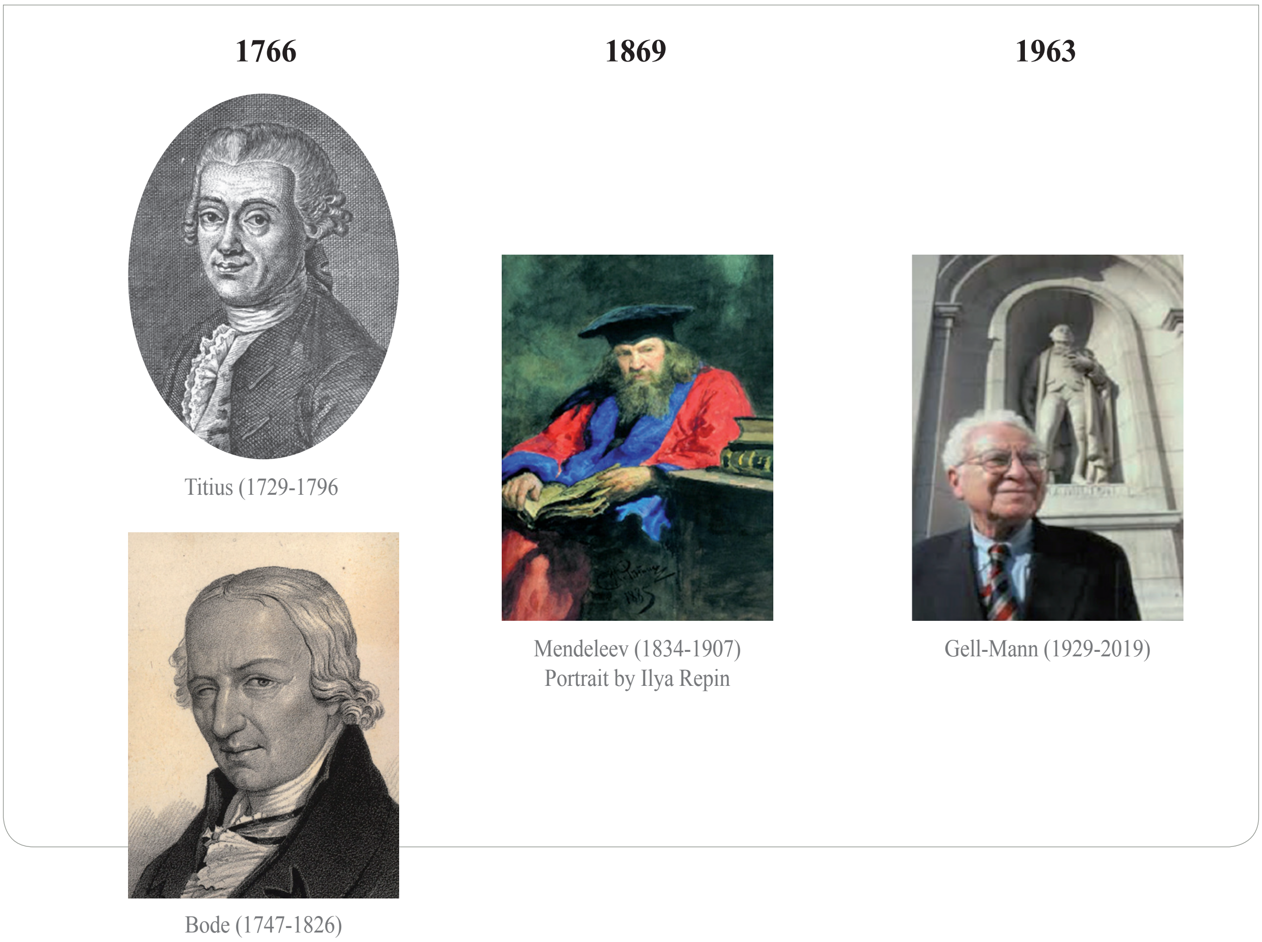



Figure 1. Three centuries of great classifiers of planets, atoms, and subatomic particles.

### 1.1. Titius-Bode

The planets describe their periodic Kepler orbits around the sun. These elliptic orbits are characterized by a major and minor axis, and an orientation in space which involves the orbital plane and the direction of the major axis. In principle Newton's gravitational law does not put limitations to the orbit parameters. In reality though, all orbits are more or less coplanar, and eccentricities are small. Most surprisingly the planets perform their journeys at regular distances from the sun, which are (approximately) described by integer numbers. This is the famous law of Titius-Bode. In a modern version [2] this law states that the length of the semi-major axis of the planetary orbits (in astronomical units) forms a geometric progression, which can be expressed as:

$$r_n = r_0 K^n \qquad (1)$$

where $r_n$ is the orbital distance of the n[th] planet, $r_0$ is the normalizing distance (0.235 astronomical units for the distance of Mercurius), and K=1.7 for our solar system (Figure 2).

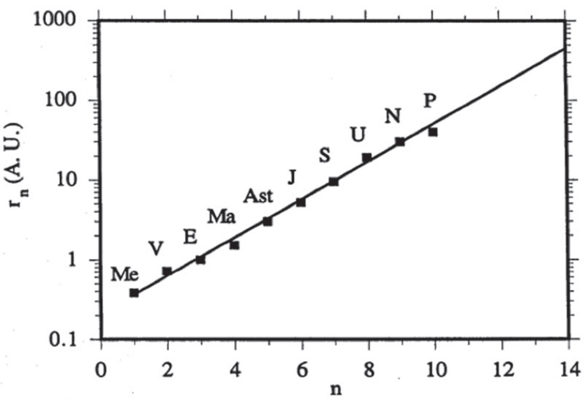



Figure 2. Geometric series of the planetary distances, from Mercurius to Pluto [2]. The astronomical unit (A.U.) corresponds to the Earth-Sun distance.

This law does not reflect a mysterious quantum condition, but goes back to the formation of the planets in the protoplanetary disk, where they ended up at regular intervals. It undoubtedly gives the whole planetary system some reassuring stability, so that we can observe our neighbours Venus and Mars passing by in the nightly sky, without fear that they are on collision course with our earth. The Titius-Bode law is an empirical rule, which has met a lot of controversy, and has even been called an example of fallacious reasoning. To this day there is no accepted rational explanation. Also, up till recently our own solar system was the only solar system known, so the law could not be corroborated by looking at other cases. This has changed and indeed the recent literature contains examples of applications of distance and period regularities according to geometric progressions [3]. In order to get the distance of Jupiter right, it was compelling to rank Jupiter as the sixth planet of the solar system, leaving a gap between Mars and Jupiter. After the discovery of Uranus in 1781, which fits into the series, the search for the missing fifth planet in between Mars and Jupiter was on, resulting in the discovery of Ceres, the largest object in the asteroid belt, in 1801.

Clearly the discovery of Titius and Bode has several characteristics that would turn up again later when Mendeleev proposed his own table: the presence of an integer number sequence, the quest for the missing element, and the initial skepticism of the scientific community. However, its true significance, which accounts for its appearance in our portrait gallery, is not so much the rule itself but the conviction that the set of the planets forms an orderly sequence, which can properly be called a ‘system’. This is a conviction that would leave its mark in Mendeleev’s discovery, and that we continue to celebrate in our lecture rooms whenever we compare the atom to a planetary system.

### 1.2. Mendeleev

Mendeleev’s table was based on empirical evidence, collecting similarities between chemical elements, in combination with approximate atomic weights. After its discovery the table met a lot of resistance and was confronted with unexpected new challenges, such as the problem of allocating the newly discovered lanthanides. The lack of a proper theoretical explanation of the periodic rule was an obvious weakness of the table, which incited critical voices. Mendeleev expressed his belief that sooner or later a suitable ‘chemical mechanics’ could see the light that would clarify the structure of his rule. Yet he could not foresee that such mechanics would require a double paradigm shift, abandoning the concept of the indivisible atom, and overruling Newtonian mechanics. This would only be realized in the first quarter of the twentieth century with the discovery of the planetary structure of the atom as a nucleus surrounded by a cloud of electrons, and the proposal of a new completely weird mechanics. [4] The quantum mechanical treatment of the hydrogen atom for the first time provides two numbers that encode the periodic system: the principal quantum number n, and the orbital quantum number l. The way in which the atomic (nl) shells are filled when running through the periods was summed up by Madelung in 1936 in a compact Aufbau rule (Figure 3):

1. *Atomic shells are filled in increasing order of the sum n+l.*
2. *For a given value of this sum, the filling is in order of increasing n.*

Already in 1930, six years before Madelung, the French engineer, entomologist, and inventor, Charles Janet had come to the same conclusion, and reordered the periodic table in the logical form of the so-called ‘left-step’ table. [5] He published his results in the obscure *Bulletin de la Société Académique de l’Oise*, and his discovery remained largely unnoticed.

As with the periodic system itself, the reception of Madelung’s rule divided the community in sceptics and believers. The sceptics point out that the Madelung rule works only partially, has many exceptions, and thus will defy all attempts to explain it. The spokesman for the sceptics is Eugen Schwarz, who claims that we should abandon the Madelung rule altogether. When discussing extensions of the periodic table up to Z=172, Pekka Pyykko notices: ‘It is almost disappointing that the simple (n+l , n) ‘Madelung rule’ still seems to hold’ [6].

Erwin Madelung
(1881-1972)

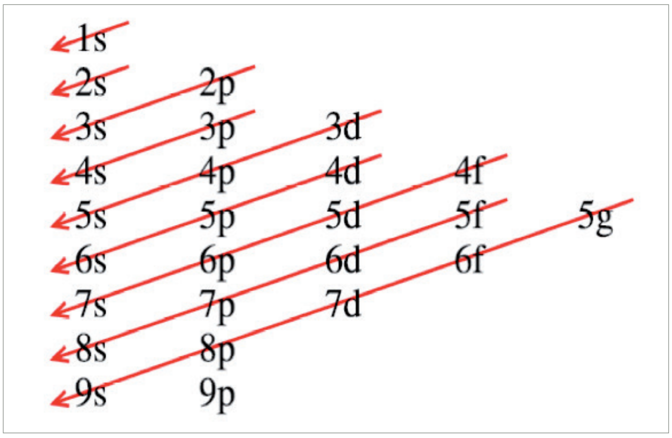



Figure 3. Filling order of the atomic orbitals, from Hydrogen ($1s^1$) up to Oganesson ($7p^6$)

In the camp of the believers probability considerations are invoked to claim that in spite of exceptions a fortuitous coincidence is ruled out. The regular numerical periodicity, expressed by the rule, must point to a hidden order, which is awaiting discovery. As for the theoretical underpinning of the Madelung rule, computational chemistry can very well provide a rigorous quantum-mechanical description of any atom, and predict properties such as spectra with an accuracy even beyond experimental resolution. The question however is to set up a general theory. This challenge was formulated by Löwdin in 1969, at the occasion of the centenary of Mendeleev's table:

> *It would certainly be worthwhile to study the (n+l , n) rule of Madelung from first principles, i.e. on the basis of the many-electron Schrodinger equation* [7].

Eric Scerri, who in his own words for many years was one of the torchbearers for Löwdin's statement, has become more sceptical towards the reductionist view in the Löwdin's challenge, which ultimately prunes the hallmark of chemistry to an exercise in theoretical physics [8].

In Section 3, we will return to Löwdin's challenge, but before this we have to make the acquaintance of the final portrait of Murray Gell-Mann, who is often referred to as the Mendeleev of the twentieth century.

### 1.3. Murray Gell-Mann

In the early nineteen sixties, the introduction of particle accelerators had yielded a plethora of so-called elementary particles, which could be grouped in families corresponding to their masses and transformations. Gell-Mann discovered that families could be identified and structured with the help of an abstract mathematical theory known as the theory of Lie groups. In Figure 4 we show one of the diagrams which Gell-Mann used to classify the baryons with rest masses between 930 to 1320 MeV/$c^2$. The technical name for this diagram is a Cartan-Weyl root diagram for a representation of the special unitary group in three dimensions, SU(3). We will explain these concepts shortly in Section 2. For now, we note that the appearance of the abstract SU(3) symmetry inspired Gell-Mann to the hypothesis that hadron matter had a composite nature and consists of truly elementary particles, which he called the quarks. The elementary basic vector was composed of three quark states: up, down and strange. The baryons are products of three quarks.

The diagram provides room for the eight hadrons in the given energy range. They include the proton and the neutron, three sigma ($\Sigma$) particles and two xi ($\Xi$) particles, and one lambda ($\Lambda$) particle. Each particle is characterized by several quantum characteristics, including charge. While the proton and neutron differ by charge, they have almost the same mass. Already in 1932 Heisenberg noticed that the proton and neutron are congeners, as if they were the two components of a degenerate quantum state, such as the up and down components of a spin state. He appropriately introduced the term isospin to express the common nature of the nucleons, which were subsequently identified as the - ½ and + ½ components of an isospin doublet [9]. The litmus test for important classifications is that they also lead to the prediction of new elements to fill the gaps that are left open by the classification. This was the case for Titius-Bode and Mendeleev, but equally so for Gell-Mann who could predict the existence of a missing member in the hadron family, and estimate an approximate energy. This time the search for this particle became at once the number one on the agenda of particle physicists. Accelerators were swiftly tuned in on the predicted energy range. It was not for long till the Omega minus particle was detected. This earned Gell-Mann rightfully the title of the Mendeleev of the twentieth century.

However, as compared to Mendeleev and his predecessors the classification of the hadrons is marked by an essential difference. In the case of the quarks, the diagrams which Gell-Mann and his contemporaries developed, present a more mature form of classification, as they combine the empirical evidence with the powerful mathematical tool of symmetry groups. The origins of this tool go back to the nineteenth century, thus predating quantum mechanics. In the next section we highlight the legacies of nineteenth century mathematicians, who provided the foundations for the use of symmetry in atomic and subatomic classifications.

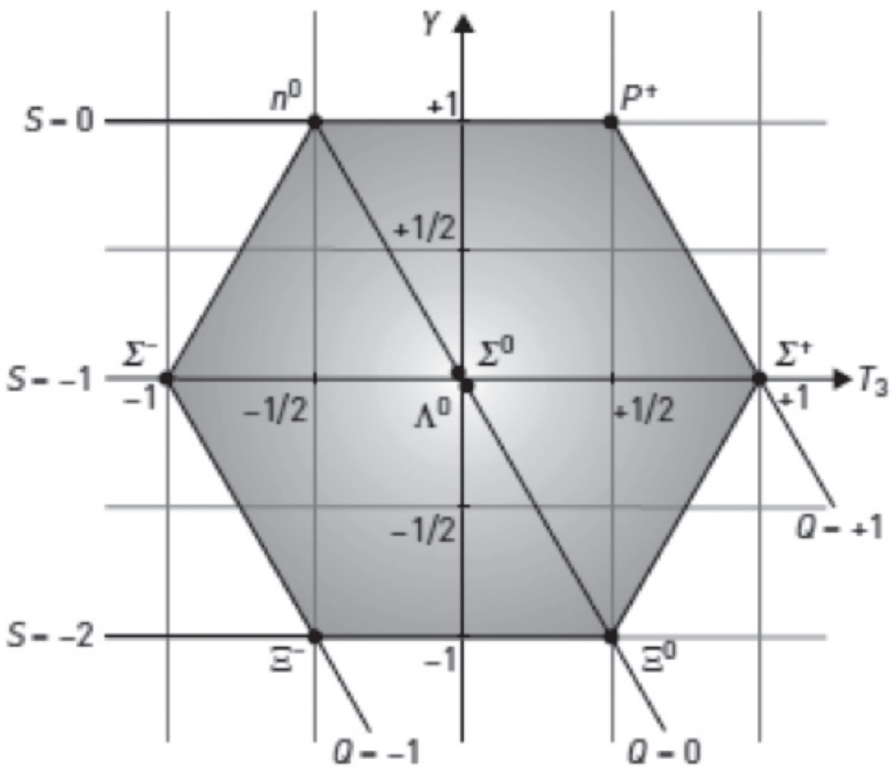



Figure 4. Cartan-Weyl root diagram for the baryon octet. Q , S, Y, and $T_3$ stand for Charge, Strangeness, Hypercharge, an Isospin component; $p^+$ and $n^0$ are the familiar proton and neutron, forming an isospin doublet. One further notices an isospin triplet ($\Sigma^-$, $\Sigma^0$, $\Sigma^+$) and another doublet at S=-2 ($\Xi^-$ and $\Xi^0$). The $\Lambda^0$-particle in the center is an isospin singlet.

## 2. The legacies

Group theory was created in a flash of genius by Évariste Galois. Its subsequent application to the symmetry of continua is due to Sophus Lie. This section is devoted to the legacies of these two towering figures of nineteenth century mathematics.

### 2.1. Évariste Galois

In 1832, when Galois died at the age of 21 in a silly duel, the world lost an exceptional mathematician and well-known revolutionary. The story is known how the night before the duel he collected all his work and left this 'lettre testamentaire' to his friend Auguste Chevalier. For a long time, his discoveries would remain a book with seven seals, but finally they found their way to the 'Journal de mathématiques pures et appliquées', founded by Joseph Liouville. Galois' discovery would inspire a whole generation of mathematicians, who developed group theory in the second half of the nineteenth century.

In his final years at the Collège Louis Le Grand in Paris, Galois was enlisted as a student of the 'Mathématiques Spéciales'. Judging from the reports by his teachers, he focused all his attention exclusively on the study of advanced mathematical problems. The problems of the day were the algebraic equations, and the possibilities to solve higher than quartic equations. Unlike his contemporaries however Galois started to play with the permutations that could be applied to the roots of the equations, and found that they form what he called a *group*.

He realized that a group is a more powerful concept than a set. We can define a set by listing its elements. So we decide which elements will belong to our set. A group is different. If we decide that two elements S and T belong to the group, automatically the consecutive actions, symbolized by products such as ST, TS, TST etc. must also be part of the group. Or, in Galois' mémoire [10]:

> *Quand nous voudrons grouper des substitutions, nous les ferons toutes provenir d'une même permutation. Comme il s'agit toujours de questions où la disposition primitive des lettres n'influe en rien dans les groupes que nous considérerons, on devra avoir les mêmes substitutions, quelle que soit la permutation d'où I'on sera parti. Donc, si dans un pareil groupe on a les substitutions S et T, on est sûr d'avoir la substitution ST.*

As an example from crystallography: if S is a fourfold rotation axis which leaves the crystal invariant, and T is a twofold rotation axis, perpendicular to S, we at once generate a group of exactly eight elements corresponding to the dihedral group, $D_4$. This result can be arrived at by a formal combination of powers of S and T, using the following simple composition rules:

$$\begin{aligned} S^4 &= T^2 = E \\ ST &= TS^3 \end{aligned} \qquad (2)$$

where E is the unit operation. Unity is restored by applying S four times, or T two times. Such rules form the 'presentation' of the group. The power of the group concept lies in the fact that the set constructs itself from the presentation, and that the result is consistent with the composition rule. By mid-nineteenth hundred the group concept got a rigorous definition and opened up a whole new branch of mathematics, focusing not only on the internal structure of groups, but also on its connection with geometry and topology. Here the work of Sophus Lie is of paramount importance.

### 2.2. Sophus Lie

The Norwegian mathematician Sophus Lie developed group theory in a direction which would be of primordial significance to twentieth century physics. As students Sophus Lie and the German mathematician Felix Klein spent the spring of 1870 together in Paris where they were introduced to the French school of analysis. Especially the work of Camille Jordan on substitution groups attracted their interest and would have a lasting influence on their careers. In a foreword to his later work on the icosahedron Felix Klein would recall that the two friends decided to split the topic between them. Lie would take the subject of continuous groups, which Klein thought of as the more difficult one, while Klein himself would focus on discrete groups [11].

> *Während ich selbst in erster Linie Gruppen discreter Operationen ins Auge fasste und also insbesondere zur Untersuchung der regularen Körper und ihrer Beziehung zur Gleichungstheorie gefuhrt wurde, hat Hr. Lie von vorneherein die schwierigere Theorie der continuirlichen Transformationsgruppen und somit der Differentialgleichungen in Angriff genommen.*

Klein's research on discrete symmetries would eventually occupy a great deal of his famous Erlangen Program. Lie's contributions in turn would have a lasting impact on physics. In the words of the French mathematician and historian of mathematics Jean Dieudonné:

> *Lie theory is in the process of becoming the most important part of modern mathematics. Little by little it became obvious that the most unexpected theories form arithmetic to quantum physics came to encircle this Lie field like a gigantic axis [12].*

In view of the crucial role which Lie theory has for our subject, we spend here a few instants to explain the basics of Lie theory, and its connection to quantum mechanics.

## 2.3. A primer on Lie algebra

Consider the dumbbell shaped $2p_x$ orbital in the xy-plane. A right-handed rotation of this function around the upright z-axis over an angle α, as shown in Figure 5, can be expressed by a matrix transformation:

$$\hat{R}_\alpha(x,y) = (x,y)\begin{pmatrix} \cos\alpha & -\sin\alpha \\ \sin\alpha & \cos\alpha \end{pmatrix} \qquad (3)$$

For our purpose the orbital functions $2p_x$ and $2p_y$ may be represented as simple Cartesian vectors pointing in the x and y directions, respectively. In Eq. 3 we have put them together in a row vector as (x,y). As the rotation proceeds, the $2p_x$ orbital transforms into $2p_x$'. The formula in Eq. 3 then describes the projection of the x' vector on the original x,y basis: the x-component decreases as cos α, while the y-component is growing in as sin α. Similarly, the $2p_y$ orbital is moving away from the y-axis. The y component now decreases as cos α. As it approaches the x-axis the x-component gains weight as - sin α. A right-handed rotation of the $2p_y$ orbital over an angle of 90 degrees will turn it into -2p .

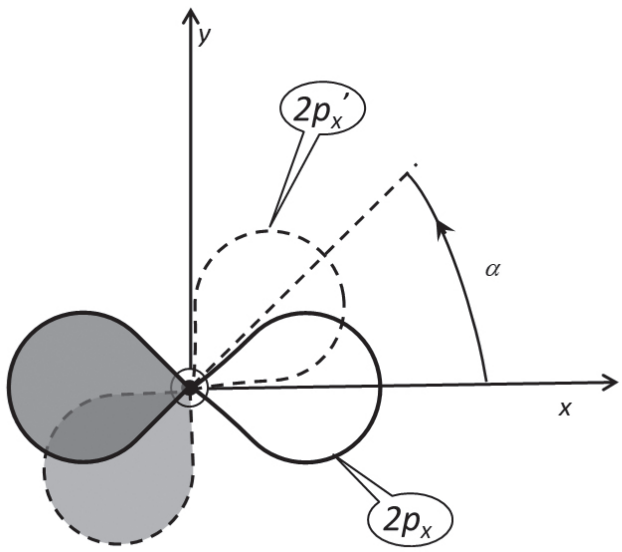



Figure 5. A right-handed rotation over an angle a turns the $2p_x$ orbital function into the dashed function, $2p_x$'

Since space is isotropic, the rotation angle is a continuous variable. It is thus sufficient to consider only a tiny rotation over an angle *d*α, since every finite rotation can be constructed from this starting point using the standard technique of the Taylor expansion. The matrix describing this infinitesimal rotation is simply obtained from the expression in Eq. 3 by taking the limit for α becoming infinitesimally small.

$$\lim_{\alpha\to 0} \hat{R}_\alpha(x,y) = (x,y)\begin{pmatrix} 1 & -d\alpha \\ d\alpha & 1 \end{pmatrix} = (x,y)(\mathbf{I}+\mathbf{X}d\alpha)$$

$$\text{with: } \mathbf{I} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix},\ \mathbf{X} = \begin{pmatrix} 0 & -1 \\ +1 & 0 \end{pmatrix} \qquad (4)$$

As this equation shows, the resulting rotation matrix approaches the sum of the unit matrix

**I** and a small increment $\mathbf{X}d\alpha$, where **X** is an antisymmetric matrix. With this result we can now introduce the *derivative* of the rotation operator, which we will represent as the *X* operator:

$$\frac{d\hat{R}_\alpha}{d\alpha} = \lim_{\alpha\to 0}\frac{\hat{R}_\alpha - \hat{R}_0}{d\alpha} \equiv \hat{X} \tag{5}$$

This operator is the backbone of Lie's algebra. Combining Eqs. 4 and 5 shows that the action of the *X* operator in function space is represented by the matrix **X**.

$$\hat{X}(x,y) = (x,y)\mathbf{X} \tag{6}$$

The key question is now: what is the *functional form* of the *X* operator? To obtain the answer, the right-hand side of Eq. 6 should also be made to terminate on (x,y), so that whatever is preceding it must be identified as the operator itself. This can easily be achieved by realizing that the unit matrix is obtained by taking the product of the partial derivative operators in a column, and the (x,y)-row vector.

$$\begin{pmatrix} \delta/\delta x \\ \delta/\delta y \end{pmatrix}(x,y) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \mathbf{I} \tag{7}$$

Adding this expression to the right of Eq. 6 yields:

$$\hat{X}(x,y) = (x,y)\mathbf{X} = (x,y)\mathbf{X}\begin{pmatrix} \delta/\delta x \\ \delta/\delta y \end{pmatrix}(x,y) \tag{8}$$

The operator function is then identified as the expression which precedes (x,y) in the right-hand side of Eq. 8:

$$\hat{X} = (x,y)\mathbf{X}\begin{pmatrix} \delta/\delta x \\ \delta/\delta y \end{pmatrix} = y\frac{\delta}{\delta x} - x\frac{\delta}{\delta y} \tag{9}$$

This is the famous Lie operator for the rotation in the x,y plane. There is a direct link between this operator and quantum mechanics. Indeed, in quantum mechanics, as in classical mechanics, a key role is played by angular momenta. The angular momentum for a rotatory movement around the z-axis is given by:

$$\hat{L}_z = xp_y - yp_x \tag{10}$$

Here $p_x$ and $p_y$ denote the components of the linear momentum. We now switch to quantum mechanics: in the Schrödinger representation of the quantum formalism the momentum operator is defined as:

$$p_x = \frac{\hbar}{i}\frac{\delta}{\delta x}, \quad p_y = \frac{\hbar}{i}\frac{\delta}{\delta y} \tag{11}$$

Substituting these operator forms in the expression for the angular momentum in Eq. 8 then yields:

$$\hat{L}_z = \frac{\hbar}{i}\left(x\frac{\delta}{\delta y} - y\frac{\delta}{\delta x}\right) = i\hbar\hat{X} \tag{12}$$

It is at once clear that the Lie operator for a rotation in the plane coincides with the angular momentum operator of quantum mechanics, except for the constant factor iħ This can be expressed in a lapidary way as: Quantum mechanics is Group Theory multiplied by the imaginary unit ánd by Planck's constant. Both factors are essential to build the bridge that connects abstract mathematics to real physics: the imaginary makes sure that the outcome of our measurements are real quantities, and Planck's constant reminds us that while mathematics does not know units, measurements never yield absolute numbers.

The results can now easily be generalized to rotations in three dimensions, and in this way we obtain a set of three Lie operators which describe the rotations in three perpendicular Cartesian planes. The corresponding Lie group is the special orthogonal group in three dimensions, denoted as SO(3).

$$\hat{L}_x = \frac{\hbar}{i}\left(y\frac{\delta}{\delta z} - z\frac{\delta}{\delta y}\right)$$
$$\hat{L}_y = \frac{\hbar}{i}\left(z\frac{\delta}{\delta x} - x\frac{\delta}{\delta z}\right) \quad (13)$$
$$\hat{L}_z = \frac{\hbar}{i}\left(x\frac{\delta}{\delta y} - y\frac{\delta}{\delta x}\right)$$

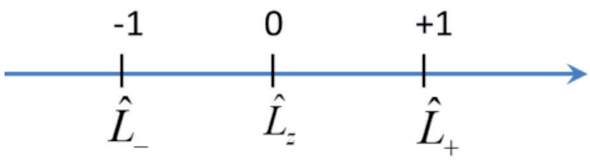
The composition rule for Lie operators is not an ordinary product but a commutator. This is denoted by square brackets. As an example the 'product' of the x and y components is worked out as follows:

$$\left[\hat{L}_x, \hat{L}_y\right] = \hat{L}_x\hat{L}_y - \hat{L}_y\hat{L}_x = i\hbar\hat{L}_z \quad (14)$$

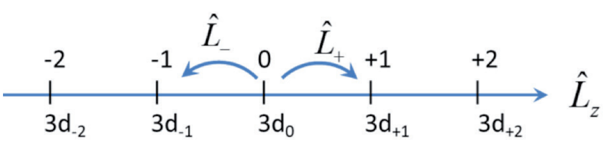
Choosing the z-component of the angular momentum as the center of this algebra, we can form linear combinations of the $L_x$ and $L_y$ components which are eigenfunctions of $L_z$, with eigenvalues +/- ħ.

$$\hat{L}_+ = \hat{L}_x + i\hat{L}_y \qquad \left[\hat{L}_z, \hat{L}_+\right] = +\hbar\hat{L}_+$$
$$\hat{L}_- = \hat{L}_x - i\hat{L}_y \qquad \left[\hat{L}_z, \hat{L}_-\right] = -\hbar\hat{L}_- \quad (15)$$
$$\left[\hat{L}_z, \hat{L}_z\right] = 0$$

This result can be represented in a one-dimensional diagram, consisting of a metric space with three points, at -1, 0, and +1 (in units of ħ), corresponding to the eigenvalues of the operators under $L_z$.




Orbitals too can be represented in such a diagram. As an example the set of the five d-orbitals appears as the row of five points indicated below. When acting on these orbitals the *L-* ,*L+* operators will act as ladder operators: they lower, increase the z-component of the angular momentum by one unit.




The resulting diagram with its shift operators that allow to jump between its lattice points is the *Cartan-Weyl diagram* for the spherical symmetry group. This is the kind of diagram that Gell-Mann used to represent the baryons in Figure 4. In that case the Lie group concerned was the special unitary group in three dimensions, SU(3). This group is more involved than the SO(3) group, since it is generated by not less than eight differential operators. It is represented by a two-dimensional Cartan-Weyl diagram with the shape of an hexagon.

Equipped with the mathematical tools that were created by Sophus Lie, and inspired by the success of Gell-Mann's approach, we can now launch the search for a covering Lie group that would encode the structure of the Periodic System.

## 3. The periodic chess board

### 3.1. APA versus EPA

To meet the Löwdin challenge two lines of attack have been proposed: the Atomic Physics Approach (APA) and the Elementary Particle Approach (EPA).

In the APA, the aim is to design a general potential energy function that incorporates the physics of the multi-electronic atom into an effective one-particle Hamiltonian and to solve the corresponding Schrödinger equation. The proponent of this approach was Valentin Ostrovsky, who elaborated the Maxwell fish-eye potential. The resulting one-particle potential equation was inserted in a Sturmian-type wave equation. A discussion of this work and a further treatment is provided in the recent literature [4,13].

The EPA approach in contrast is inspired by Gell-Mann's work and calls for an elementary particle corresponding to a symmetry group, the modes of which present the chemical elements. This is the approach which we have used in our recent monograph [1], and that will be pursued in this section.

Before starting our exploration, it is well to remind us of the possible pitfalls and traps that are laid out on our journey. Ostrovsky sends us an advance warning in a vehement attack on the EPA approach [14].

*It seems that the abstract group-theoretical approach, as currently developed, amounts to a translation of empirical information on the periodicity pattern for atoms in a specialized mathematical language – but no other output is produced. Probably this approach would have explanatory power only within a community which speaks this language.*

While we maintain that group theory offers a most powerful tool to unveil Nature's secrets, we should not be blind for the danger of purely formal approaches that may have an aesthetic appeal but lack real content.

It is thus of crucial importance to clearly state the requirements that an EPA approach of the elements should obey:

- The proposed symmetry should include the spherical symmetry of the atom as a subgroup
- The proposed symmetry should have the SO(4,2) non-invariance group of the hydrogen atom as its covering group
- It should recognize the parity of n+l as a quantum characteristic which explains the period doubling, as shown in the left-step table
- The approach should offer an insight into the Madelung rule

### 3.2. SO(4,2) group

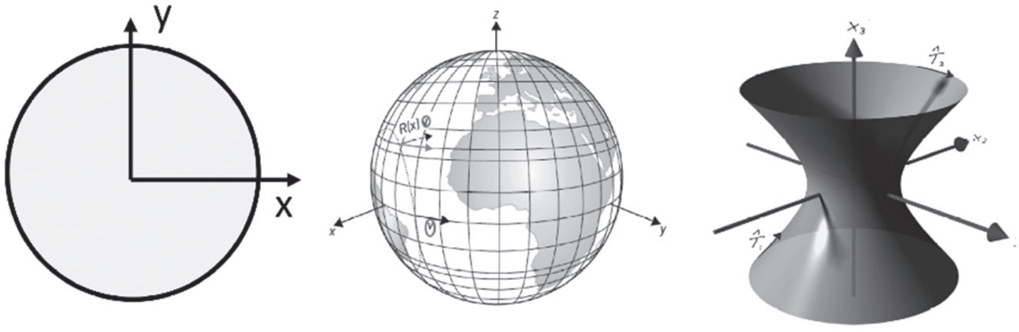
Our first task will be to explain what is meant by the SO(4,2) non-invariance symmetry group, which covers the full hydrogen spectrum. SO(n) stands for special orthogonal groups, these are Lie groups that describe rotations about a fixed point in n-dimensional space. So SO(2) is the rotational symmetry of a circle. SO(3) collects the points at a given radius of a fixed origin, in other words it is the symmetry of a sphere. In coordinate space SO(3) thus conserves the norm of a vector:

$$x^2 + y^2 + z^2 = a \qquad (16)$$

where $a$ is a constant.

This is the symmetry group that generates the spherical harmonics, characterized by the orbital quantum number l. Obviously, atoms have spherical symmetry and thus exhibit harmonic states. But, in the case of hydrogen, its spectrum reveals the presence of a deeper symmetry. Indeed the state energies of hydrogen only depend on the principal quantum number n, and not on l. So 2s and 2p share the same energy, in spite of their different shapes. The hidden symmetry group that explains this unexpected degeneracy is the hyperspherical symmetry group SO(4), describing rotations in 4 dimensions. This group was identified by Fock in 1935. However, already in 1926, Pauli had derived an operator algebra that generates the hydrogen spectrum. [15] While deriving his result Pauli in fact unknowingly reconstructed the Lie group SO(4) of the hypersphere. Years later Gell-Mann would accomplish the same remarkable exploit by reinventing SU(3) symmetry to tackle his hadronic conundrum.

The three-dimensional sections of a hypersphere are perfect spheres with varying radii, exactly as the two-dimensional sections of a sphere are circles with varying radius. The hyperspherical symmetry group is based on six rotation operators: the three angular momentum operators, and three more operators corresponding to the Cartesian components of the Runge-Lenz vector. The latter vector is less well known than the angular momentum vector, but an equally important kinematic quantity. In fact, it also plays a determining role in the classical central field problem. Consider the Kepler orbit of a planet in the gravitational field of the sun. The planet describes an ellipse with the sun in a focus point. The angular momentum is a vector perpendicular to the orbital plane. Its conservation implies the invariance of the orbital plane. The Runge-Lenz vector is a vector oriented along the major axis of the ellipse. Its conservation implies that the orientation of the ellipse in the orbital plane is invariant as well. It thus prevents the precession of the planetary orbit. As Pauli showed, the quantum-mechanical expression of these invariances leads directly to the hydrogen spectrum.




$$x^2 + y^2 = a \qquad x^2 + y^2 + z^2 = a \qquad x^2 + y^2 - z^2 = a$$

Figure 6. Lie groups of the circle, SO(2), a sphere, SO(3), and a hyperboloid, SO(2,1).

If in Eq. 16 we replace $z$ by $iz$, the conserved quantity becomes:

$$x^2 + y^2 - z^2 = a \qquad (17)$$

The result of this transformation is to open up the sphere at its poles to form an open ended hyperboloid, as shown in Figure 6. Its horizontal cross sections are circles, while its vertical sections are hyperboles. The x and y coordinates thus continue to be 'space-like' while the z coordinate runs from -∞ to +∞, and is said to be 'time-like'. The orthogonal group which describes this surface is denoted as SO(2,1).

This brings us finally to the group SO(4,2). The notation indicates that it contains the four space-like coordinates of the SO(4) group, and in addition two time-like degrees of freedom. These additional degrees of freedom acts as rescaling factors, which change the metric of the atomic space, and as a results compress the spectrum of bound energy states of hydrogen, which covers a range of 13.6 eV, to a single infinitely degenerate level. The operators of SO(4,2) allow to travel freely in this space and thus move from one state to another.

The Cartan-Weyl diagram of SO(4,2) is now a three-dimensional polyhedron, viz. a cuboctahedron. It thus has a richer topology than the two-dimensional hexagon of Gell-Mann's space. For our purposes we can project this diagram in a plane, where it assumes the format of a periodic chess board, with n rows and l columns, as shown in Figure 7.

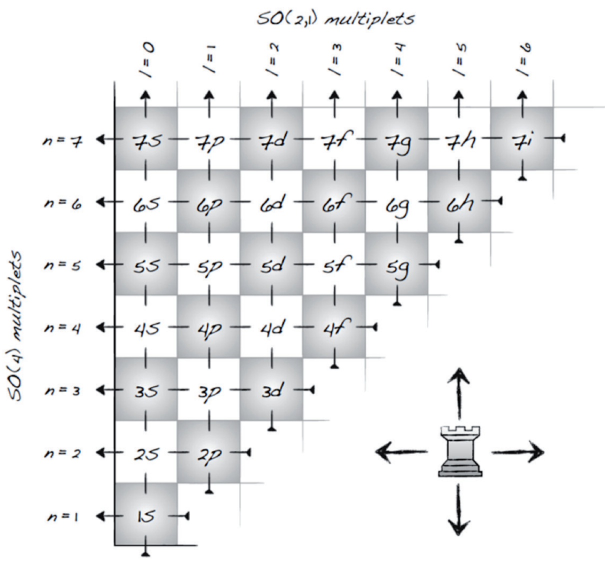



Figure 7. Representation of the periodic system on a chess board, where each entry contains the entire set of orbitals of nl type.

Each entry on this board corresponds to the set of 2l+1 orbitals with a given principal quantum number n and orbital quantum number l. As an example in the 2p slot of the chess board are thus located the three orbitals $2p_x$, $2p_y$, and $2p_z$. The covering Lie group of hydrogen offers an unexpected new perspective on the periodic system*: it appears as the projection of a Cartan-Weyl diagram of SO(4,2)*. As the pieces move over this chess board, the operators of our covering group jump from state to state. To each of the chess pieces correspond particular symmetries. The royal pieces King and Queen perform all possible moves and thus represent the parent group itself. As indicated in Figure 7 the rooks move vertically, changing the principal quantum number, or horizontally changing the orbital quantum number. To these moves correspond the subgroups SO(2,1) and SO(4) respectively.

### 3.3. The Madelung rule

Now we have to define precisely what is understood by the symmetry of the Madelung rule. This can be achieved with the help of the correlation diagram in Figure 8. The vertical axis represents a linearized energy scale, which is simply proportional to the principal and orbital quantum numbers. The coordinates of a given (n,l) point are then read off as :

$$E(n,l) = n + xl \tag{18}$$

where $x$ is varied in the diagram from -1 to +1. The centre of the diagram, with $x$=0, represents the hydrogen levels, determined uniquely by the principal quantum number. On the right is depicted the limiting case with $x$=+1, where the energy is determined by the plain sum n+l. This limit corresponds to Madelung's first rule, which collects all levels in multiplets, characterized by the same sum value. Madelung's second rule tells us that this is an ideal limiting case, whereas the actual periodic system is situated in between the hydrogen and Madelung limits, but close to x=+1.

As was argued before degeneracies are hallmarks of underlying symmetry groups. Clearly the degeneracy in the centre of the diagram reflects the SO(4) symmetry of hydrogen. Likewise we define the *symmetry group of the periodic system* as the group that is responsible for the degeneracy pattern observed at x=+1, which is the ideal case predicted by Madelung's first rule. The second rule then represents a breaking of this symmetry.

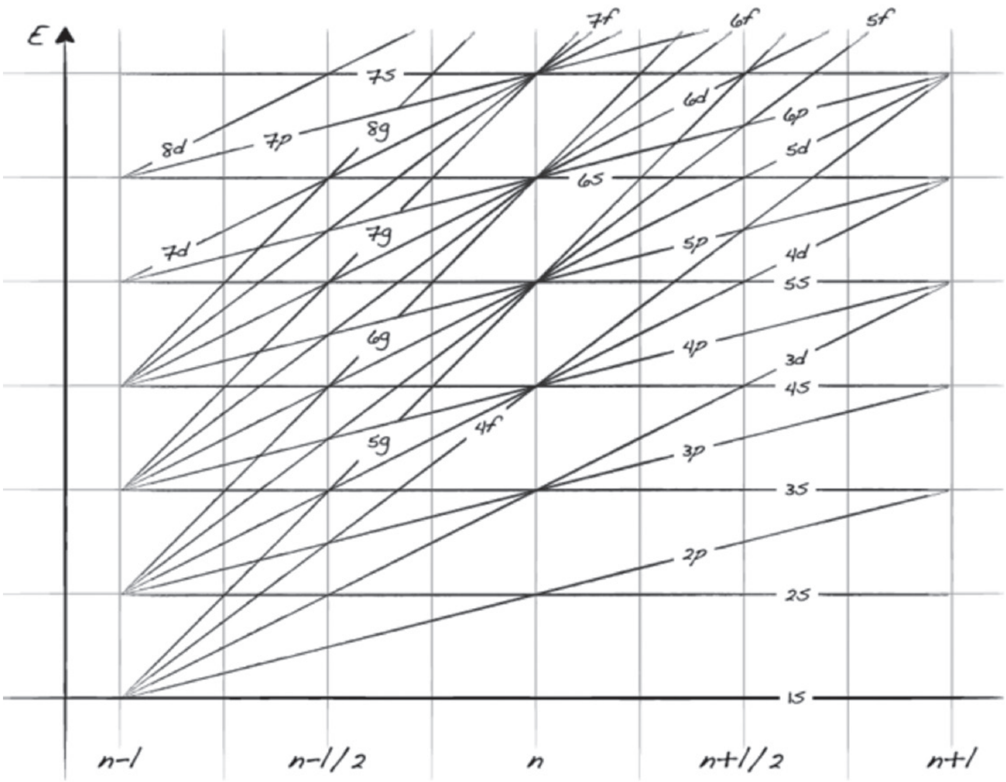



Figure 8. Linearized correlation diagram between the principal and orbital quantum numbers.

In the EPA approach the Löwdin challenge thus boils down to finding the algebra that generates Madelung's first rule.

It is also interesting to examine the opposite side of the diagram, with x=-1, where the level energy is determined by the difference n-l. This quantization represents a kind of anti-Madelung sequence, which we have termed the Regge sequence, after Tullio Regge (1931-2014) who introduced the concept of trajectories in scattering theory. Resonances in this theory correspond to sequences of hadronic particles, represented by the strings on the left of the diagram.

### 3.4. The chiral bishop

Returning now to the periodic chess board, it is observed that the Madelung and Regge multiplets correspond to the diagonals on the chess board. The pieces that move along these diagonals are the bishops. These are the only monochromatic pieces on the board, meaning that they are bound to either the white or the black squares, where they will spend all their life, *depending on the parity of n+l*, as shown in Figure 9.

Vector operators that correspond to the moves of the bishop define a Lie algebra, corresponding to the SO(3,2) symmetry group, which is a subgroup of SO(4,2). By confining the moves to diagonal displacements the parent group is thus broken. Under SO(3,2) the (n,l) states can only be connected to states with the same parity of n+l. Under this symmetry lowering the whole chess board is split up into a white and a black subboard, which are copies of each other. This splitting explains straight away the apparent doubling of the periodic table under the Madelung rule.

On the right of Figure 9 the black and white diagonals are displayed separately in tabular form according to their Madelung parity. This gives rise to the so-called left step table of Charles Jannet, with

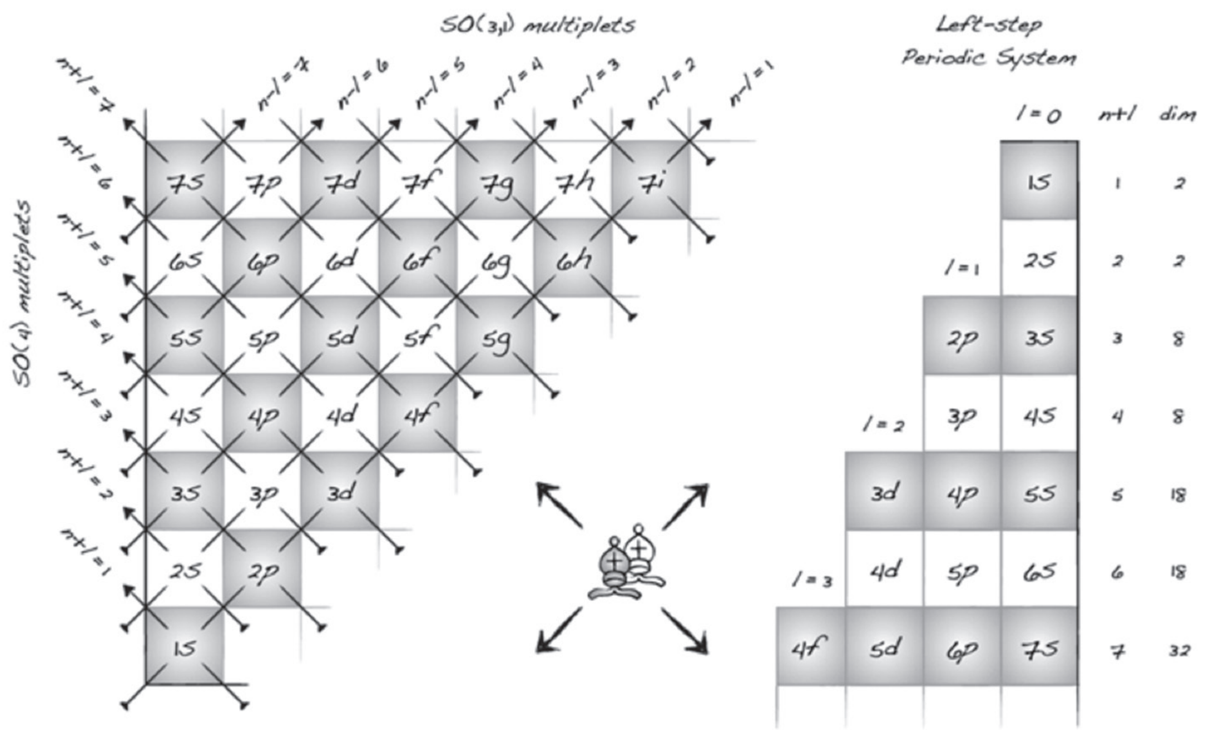



Figure 9. Moves of the bishops on the chess board preserve the sum or difference of the n and l quantum numbers, corresponding to Madelung or Regge sequences respectively.

a strict sequence of row dimensions as: 2, 2, 8, 8, 18, 18, 32 ... Note that in this table $(2s)^2$, Beryllium, is placed under the $(1s)^2$ element, Helium.

While SO(3,2) provides a quantum characteristic for the doubling of the table, it falls short of reaching our final goal to find a Lie group that matches Madelung's first rule. To achieve that goal, one should construct operators that separate Madelung and Regge directions, as shown in Figure 10. We call such operators that run only either along the Madelung, or along the Regge sequences 'chiral' bishops.

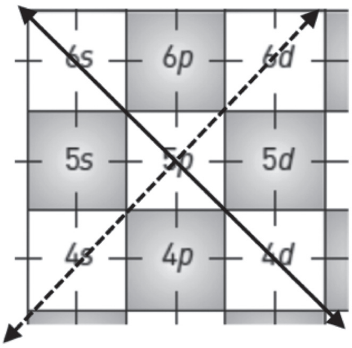



Figure 10. Action of the chiral bishops on the periodic chess board: the Madelung operator runs along the solid diagonal (here with n+l=6), the Regge operator runs along the dashed diagonal (here with n-l=4)

Now the crux of the problem is that it is simply impossible to construct such chiral operators in SO(4,2)! If we look at the diagonal operators in this group they will always be achiral, i.e. they always induce jumps along both diagonals *simultaneously*, as illustrated in Figure 11. As the figure further shows, by making linear combinations of these achiral operators we can choose to proceed upwards (or downwards), but it is simply impossible to direct them uniquely along the Madelung (or Regge) diagonal.

So the path to a Madelung subgroup within SO(4,2) is blocked. The reason is that while SO(4,2) contains an operator that yields the value of the principal quantum number n, it lacks an operator that recognizes the angular quantum number l. Instead the angular momentum is obtained by acting with the operator $L^2$, which has eigenvalue l(l+1). This is not quite the same as a direct measure of the value of l. For instance, the eigenvalue of the $L^2$ operator is always even, so this operator is not able to determine the parity of l. To overcome this problem, an additional operator is introduced which allows us to access the orbital quantum number directly. This operator is denoted by Englefield as $S$ (not to be confused with the spin operators) [16].

$$\hat{S}\left|nlm_l\right\rangle = \left(l+\frac{1}{2}\right)\left|nlm_l\right\rangle \qquad (19)$$
$$\hat{S}^2 = \hat{L}^2 + \frac{1}{4}$$

The $S$ operator is outside SO(4,2). The commutation of $S$ with the operators of SO(4,2) will produce an entirely isomorphic copy, which we will denote as the primed algebra SO(4,2)'. The combination of these two algebra's yields a group structure which now indeed produces the desired chiral bishops, as indicated in Figure 12.

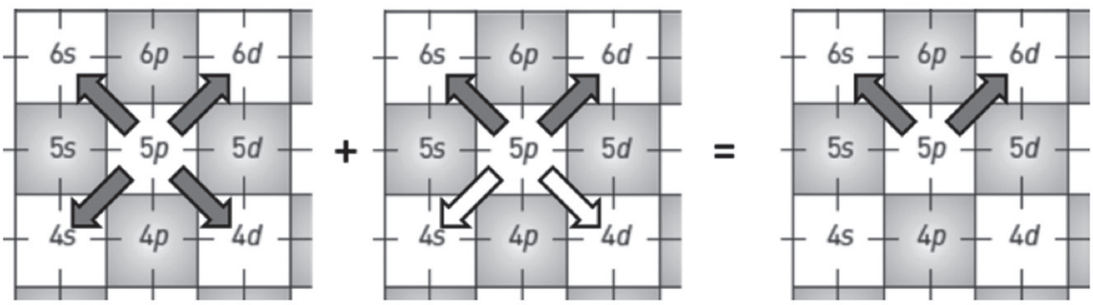



Figure 11. Combination of achiral diagonal moves yields an achiral result. (Black and white arrows have the same magnitude but a different sign. Their sum thus vanishes)

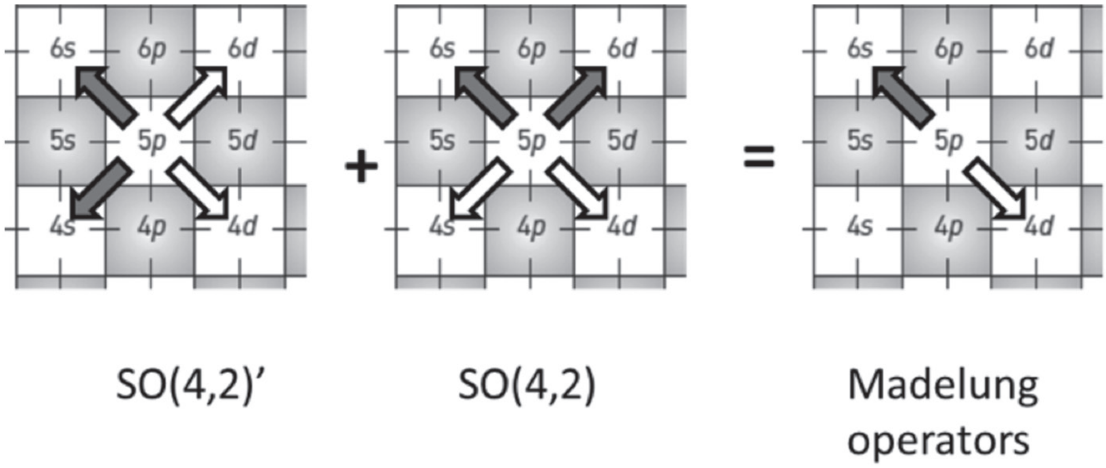



Figure 12. The addition of achiral diagonal moves from the primed and unprimed SO(4,2) yields a chiral result, which corresponds to the Madelung operators

The Madelung operators which are obtained in this way are again vector operators, and will be denoted as $M_x$, $M_y$, $M_z$. In all we obtain now a group structure which consists of six operators: the three Madelung operators, and the three angular momentum operators. The corresponding algebra now reads:

$$\begin{aligned}
&\left[\hat{L}_i, \hat{L}_j\right] = i\varepsilon_{ijk}\hat{L}_k \\
&\left[\hat{L}_i, \hat{M}_j\right] = i\varepsilon_{ijk}\hat{M}_k \\
&\left[\hat{M}_i, \hat{M}_j\right] = i\varepsilon_{ijk}\varsigma_M \hat{L}_k \\
&\text{with: } i,j,k = x,y,z
\end{aligned} \tag{20}$$

where $\varepsilon_{ijk}$ is the antisymmetric tensor, i.e. it is +1 for even permutations of the three labels *ijk*, and -1 for odd permutations. This algebra is entirely similar to the SO(4) algebra of hydrogen, except for the appearance of an extra factor $\zeta_M$ in the commutators of the Madelung operators. This factor is equal to:

$$\varsigma_M = \frac{n - l - \frac{1}{2}}{l + \frac{1}{2}} \tag{21}$$

Because of this factor the resulting algebra is non-linear. Indeed to obtain this factor requires the extra operators that produce n and l, in other words the commutator is not a linear function of the $L_k$ operator, since the preceding factor is a ratio of operators. Otherwise this group has SO(3) symmetry as a legal subgroup, thus fulfilling an essential requirement. The search for the group-theoretical expression of Madelung's first rule thus has turned up an unexpected algebraic structure, which goes beyond the standard linear Lie algebras. In the final section we will reflect on the physical meaning of this result.

## 4. Conclusions

Around the time that Mendeleev was publishing his far reaching taxonomy of the chemical elements, two young mathematicians, Sophus Lie and Felix Klein, met in Paris, and got under the spell of a new branch of mathematics: group theory. They made plans for the further development of Galois' legacy, but it would still take more than half a century before the legacy of Évariste Galois and Sophus Lie would show up in the physical sciences. A milestone in this respect was the demonstration of the hyperspherical symmetry of hydrogen by Vladimir Fock in St. Petersburg in 1935. Algebra's were developed and applied by theoretical physicists such as Pascual Jordan, Paul Dirac, and Eugene Wigner.

A Lie group was also at the centre of Gell-Mann's classification of the elementary particles, which made him the Mendeleev of the twentieth century.

Since then the question arose if a similar structure could be at the basis of Mendeleev's periodicity rule, and what would be its physical implications.

The SO(4) like algebra, which we arrived at in the previous section, deviates from the standard linear structure. What does this mean? Since its structure is entirely isomorphic to Pauli's and Fock's SO(4) algebra for the hydrogen problem, except for the appearance of the $\zeta_M$ function, it entices a comparison between hydrogen and poly-electronic atoms. Both are central field problems. In hydrogen the field originates from the Coulombic attraction of the nuclear charge, and this is expressed by the linear SO(4) algebra. In poly-electronic atoms the configuration of the outer electron is determined by the combination of the nuclear attraction and the repulsion by the electron cloud. In the limiting case of Madelung's first rule, the central field quantization replaces the principal quantum number by the sum of radial and orbital quantum numbers. This is matched by the replacement of the linear SO(4) algebra by a deformed one. The special structure of this algebra implies that space itself is transformed, because of the presence of the electronic cloud. Such a transformation is a conformal mapping. It incorporates the electronic repulsion into the structure of atomic space itself, and thus leads to an integrated approach of the central field, as if it were due to a single pseudo-particle. Further advances aim at developing a quantum-mechanical formalism which incorporates this mathematical structure [13]. In the end this should lead to the reconciliation between the EPA and APA approaches.

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