The 'Chemical Mechanics' of the Periodic Table

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1 Introduction

In 1969, the centennial of Mendeleev's discovery of the periodic table was commemorated by an international conference devoted to the periodicity and symmetry of the elementary structure of matter. It was held in the Vatican and brought together a selected audience of first-rate atomic and nuclear scientists. In 1971, the proceedings were published in a joint publication of the *Academy of Sciences* of Torino and the *National Academy* in Rome.[1]

Among the many interesting contributions, the American cosmologist John Archibald Wheeler described a mind-boggling journey from 'Mendeleev's atom to the collapsing star'. According to Wheeler, Mendeleev was convinced that the atom is not 'deathlike inactivity' but a dynamic reality and Mendeleev expressed his hope that the discovery of an orderly pattern would 'hasten the advent of a true chemical mechanics'.[2]

This hope has certainly been met by Schrödinger's wave mechanics, which provides an accurate tool to simulate the properties of the elements. However, the overall structure and symmetry of the periodic table continues to defy understanding. The quest for an effective universal force law at the basis of the mechanics of multi-electron atoms forms the topic of this contribution.

2 Bertrand's Theorem

The search for central force laws should start with Bertrand's theorem in classical mechanics. In 1873, the French mathematician Joseph Louis Bertrand presented to the Paris Academy a short note on central force laws that give rise to stable orbits.[3, 4] For a proper understanding of the research question which Bertrand was addressing, we start from an everyday experiment. A mass attached to a string can easily be swept around in a perfectly circular orbit by simply pulling on the string. The only requirement is that the force should be fixed and directed towards the center of the orbit. If we want the mass to go faster, we simply have to pull harder. Newtonian mechanics tells us that there exists a simple relationship between the centripetal force, F, which we have to exert, and the speed of revolution, v:

$$F = \frac{mv^2}{r}. \tag{1}$$

Here m is the mass and r is the radius of gyration. So if the string is longer and the force stays the same, the mass will reach a higher speed. As this simple experiment shows, a fixed central attraction force can give rise to a closed circular orbit, provided the speed of revolution and the radius are in line with Eq. (1). However, the resulting orbit is 'fragile'. Any change of F, v, or r leads to a loss of stability, which often results in chaotic behavior.

What Bertrand was looking for are attraction forces for which a body, launched arbitrarily with a speed less than a certain limit and pulled towards a given center, *necessarily* describes a closed curve about this center. In the solar system, the planets are attracted to the center of mass of the system by

the gravitational force, and — happily for us — the solar system is robust and does not collapse but maintains stable orbits for ages. To guarantee the stability of such a system, we cannot invoke a fixed stable force, nor invisible ropes of a constant length; we need 'force laws', which impose a functional form that relates the attraction force to the distance. Bertrand's communication to the Academy, which is since then known as Bertrand's Theorem, proved that there are only two force laws with this property:

1. Newton's law of gravitation where the force is inversely proportional to the square of the distance to the center,

2. A central force which is directly proportional to the distance to the first power.

Both these laws are treated by Newton in his *Principia*.[5] The law of gravitation gives rise to the Kepler orbits, which are ellipses with the center of attraction in one of the focal points of the ellipse. Bertrand called this law 'the one from Nature', since it describes the stability of the solar system. Later on, exactly the same distance dependence was found to be valid for the electrostatic attraction between point charges of opposite sign, as expressed in Coulomb's law. This attraction force gives rise to a potential which is inversely proportional to the distance $\sim 1/r$, as shown in Figure 1.

The second law, which Newton lapidary expressed as 'the force is as the distance', is in fact a generalization of Hooke's law, which states that in a spring the elastic restoring force for small distortions from the equilibrium is simply proportional to the extent of elongation or contraction. It gives rise to the harmonic oscillator, the three-dimensional form of which is the spherical oscillator. The corresponding potential is a parabolic, as shown in Figure 2.

In this case, Newton demonstrated that an elliptic orbit, with the center of attraction in the center of the ellipse, requires a centripetal force which is proportional to the distance. As a corollary he also noted the 'inverse problem' that such a force must give rise to elliptic orbits, at least if the
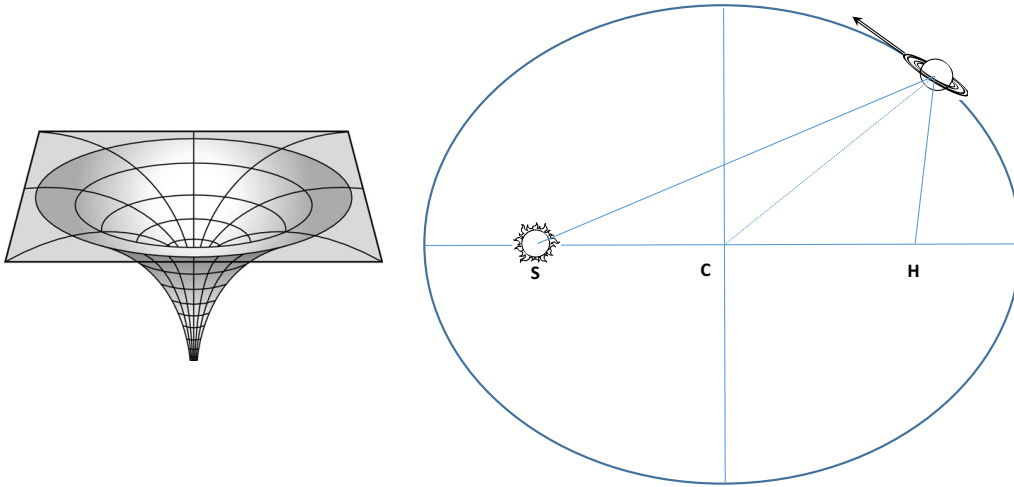
Figure 1: Left: the attraction potential corresponding to an inverse square force law. Right: the corresponding orbit is an ellipse with the attraction hole in one of the focal points.

velocity is below the escape limit.

Hence both cases give rise to elliptical orbits, but with different symmetries: the Kepler orbit has a line of symmetry along the major axis of the ellipse, while the oscillator orbit has two lines of symmetry along the major and minor axes of the ellipse. In fact, Newton observed that these two unique potentials are to a certain extent each others dual.[6] We briefly present Newton's result in the Appendix.

3 Quantum Mechanics

3.1 Stability and conservation

The two cases distinguished by Bertrand in classical mechanics also are paradigmatic in quantum mechanics. The analogue of the planet gravitating around the sun on Kepler orbits is of course Schrödinger's hydrogen atom, with gravity being replaced by the purely electrostatic Coulomb attraction, and the negatively charged electron 'orbiting' the positively charged nucleus.
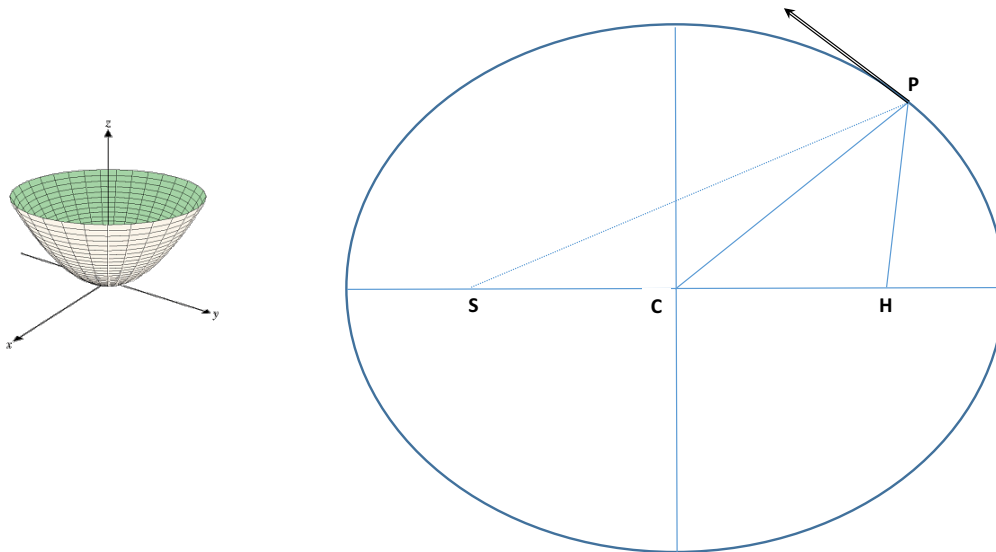
Figure 2: Left: a parabolic attraction potential corresponding to a force proportional to the distance. Right: The corresponding orbit is an ellipse with the attraction hole in the center.

The analogue of the force-equals-distance law is the quantum mechanical spherical oscillator which is ubiquitous in physics, and which furnished the model potential on which the quark model of Gell-mann was based. Not surprisingly then, the harmonic oscillator is often called 'the mother of all quantum systems.'

But what is so special about these two cases, which link the macrocosm of classical mechanics to the microcosm of quantum mechanics? Both cases stand out because in both cases the motions of the orbiting particle conserve quantities, that in turn explain the stability of the orbit. In the case of the Kepler system the conserved quantities are the angular momentum and the Runge-Lenz vector. Both are vectorial quantities and thus involve each three Cartesian components.

The angular momentum is a vector which is perpendicular to the orbit and thus conserves the plane of revolution. In order to destabilize this plane, an extra torque force should be exerted. This explains why the planetary

orbits have not deviated much from a common ecliptic plane since the origin of the solar system. The special feature of the Kepler orbit, however, is the conservation of an extra vectorial quantity, known as the Runge-Lenz vector (or the Hermann-Bernoulli-Laplace-Hamilton-Runge-Lenz vector to be historically correct).[7] This vector is perpendicular to the angular momentum and points along the major axis of the ellipse. Conservation of this vector implies that the in-plane orientation of the ellipse is maintained and that the precession of this orientation due to many-body effects is damped.[1]

In quantum mechanics both these quantities are replaced by three operators which commute with the Hamiltonian. The set of these six operators forms an algebra, which has been identified as the algebra of the SO(4) Lie group, standing for the special orthogonal group of rotations in four dimensions. The principal quantum number n is an eigenvalue of this algebra, and takes on the values:

$$n = 1,\ 2,\ 3,\ \ldots,\ \infty. \tag{2}$$

If the algebra is limited to the three angular momentum operators only, the group is reduced to the SO(3) group, which is the symmetry of a sphere in three dimensions and reflects the obvious spherical symmetry of the problem. It gives rise to the orbital angular momentum quantum number l, which stands for the angular dependence of the orbits. The l quantum number takes on the values from zero to a maximum of $n - 1$ in integer steps. For any given value of n, there are therefore n values of l:

$$l = 0,\ 1,\ 2,\ 3,\ \ldots,\ n - 1.$$
$$s,\ p,\ d,\ f,\ \ldots \tag{3}$$

Hence, in wave mechanics the trajectories of the electron no longer follow planetary orbits, but the connection is maintained through the conserved quantities.

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[1]If the major and minor axes of the ellipse would not retain their fixed orientation in the plane, the orbit would no longer be closed. The major axis would start to precess, and a 'rosette' would be traced out over time. The orbit is then said to be space-filling.

Similar analogies can be drawn between the spherical oscillator in classical and quantum mechanics. In this case, conserved quantities can be gathered in a Lie algebra with eight operators, which generate the SU(3) group. This is an acronym for the special unitary group in three dimensions. We will not consider this further in the present context. Both the SO(4) and SU(3) algebras are prime examples of Lie algebras. They explain why the corresponding problems can be solved exactly, and their solutions have given us the quantum numbers that describe the physical states of the hydrogen atom and quark matter. In fact, much of the success of quantum mechanics is due to the exact solvability of these simple model systems, and the quantum numbers coming out of these treatments play an undeniable key role in the whole of physics.

3.2   Force laws and quantum numbers

But this is not all. There is still a deeper connection between the force laws and the quantization. This stems from a separate consideration of the radial and angular components of the momentum. In the hydrogen atom, the energy is inversely proportional to an integer number n, which is the principal quantum number. It is given by:

$$n = 1 + n_r + l. \tag{4}$$

Here n_r is the radial quantum number and l corresponds to the angular or orbital quantum number. The radial quantum number n_r counts the number of radial phase changes of the wavefunction when going from $r = 0$ to $r = \infty$. As an example: the $1s$ orbital is described by a monotonously decreasing exponential, having a cusp at the origin and approaching a zero asymptote towards infinity. This function has no radial nodes and thus $n_r(1s) = 0$. For the $2s$ orbital there is one sign change in the radial interval, and hence $n_r(2s) = 1$, and so on, yielding: $n_r(ns) = n - 1$.

The orbital quantum number l counts the number of angular nodes. These are recognized by the presence of nodal planes in the orbital graphs. The

Table 1: Radial and angular quantum numbers, n_r and l, for the states of the hydrogen atom and the spherical oscillator.

	Hydrogen				Oscillator		
	n_r	l	n		n_r	l	n
$1s$	0	0	1	$1s$	0	0	0
$2s$	1	0	2	$1p$	1	0	1
$2p$	0	1	2	$2s$	0	1	2
$3s$	2	0	3	$1d$	2	0	2
$3p$	1	1	3	$2p$	1	1	3
$3d$	0	2	3	$1f$	0	2	3
$4s$	3	0	4	$3s$	2	0	4
$4p$	2	1	4	$2d$	1	2	4
$4d$	1	2	4	$1g$	0	4	4
$4f$	0	3	4				

$2p_z$ orbital has a different sign on the northern and southern hemisphere, and hence becomes zero in the equatorial plane. Consequently one has: $l(2p_z) = 1$. An orbital such as d_{xz} obviously has two orthogonal nodal planes, one coinciding with the equatorial xy-plane, the other being the upright yz-plane. In more complicated cases such as d_{+2} or d_{z^2} it becomes less obvious to delineate these phase changes, and the application of the angular momentum operator is required. The contributions of n_r and l to the principal quantum number of hydrogen are listed in Table 1.

The fact that both quantum numbers appear with the same weight in Eq. (4) can be understood when transposing it to the classical limit. It then means that the "frequency of revolution is the same as the frequency of excursions in the radial direction". This is self-evident for the ellipse in
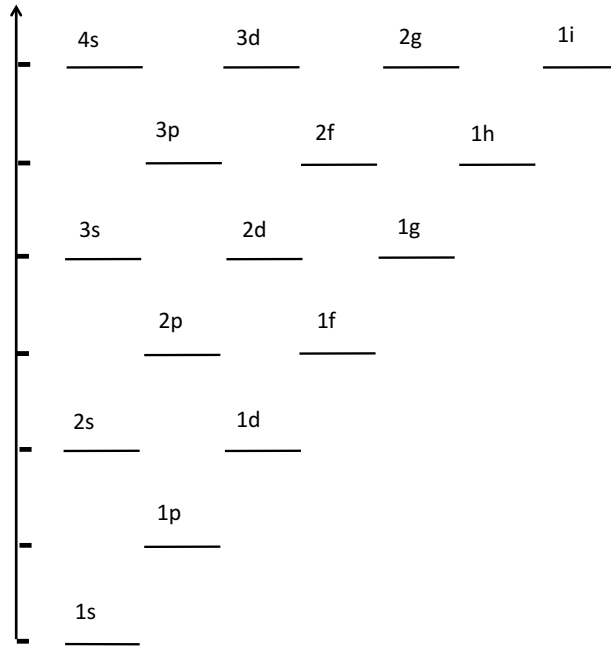
Figure 3: Energy spectrum of the spherical oscillator.

Figure 1 with the center of attraction in one of the focal points. One full turn around the perimeter will visit the perihelion point exactly once.

For the harmonic oscillator, the energy eigenvalues in units of $\hbar\omega$ are determined by a different expression:

$$E = 2n_r + l + \frac{3}{2}. \tag{5}$$

Here the term $3/2$ is the zero-point energy of the oscillator. The sum $2n_r + l$ corresponds to the number of boson excitations. The states of the oscillator are also listed in Table 1, and the spectrum is shown in Figure 3. Since now the radial frequency appears with a double weight, the same extrapolation will dictate that the radial frequency is twice as large as the angular one. Hence for the classical elliptic trajectory, when going around the center once, the shortest distance to the center will be visited twice, as is precisely the case for the elliptical orbit in Figure 2 with the attraction center in the origin.

4 The chemical orbit

This is precisely the point where Wheeler steps in.[2] For him, the chemical mechanics, which finds its expression in the periodic table, is not limited to the quantum mechanics of the hydrogen atom, but points to a more universal force law, at the basis of the internal symmetry of the periodic system. Crucial to this chemical mechanics, according to Wheeler, is the so-called 'Madelung rule', to which we turn next.

4.1 The Madelung rule

The Madelung or $(n + l, n)$ rule was discovered in 1936 by the German physicist Erwin Madelung, and is generally defined as follows:

Definition 4.1. (The Madelung $(n + l, n)$ rule): With increasing nuclear charge Z, one-electron orbitals are filled according to increasing $N = n + l$, with n the principal quantum number and l the orbital quantum number. For fixed N, the orbitals are filled in order of increasing n. $\qquad\square$

Application of the $(n + l, n)$ rule gives rise to the following orbital sequence:

$$\underbrace{\overbrace{\{1s\}}^{n+l=1}}_{\text{dim}=2} \ll \underbrace{\overbrace{\{2s\}}^{n+l=2}}_{\text{dim}=2} \ll \underbrace{\overbrace{\{2p < 3s\}}^{n+l=3}}_{\text{dim}=8} \ll \underbrace{\overbrace{\{3p < 4s\}}^{n+l=4}}_{\text{dim}=8} \ll \underbrace{\overbrace{\{3d < 4p < 5s\}}^{n+l=5}}_{\text{dim}=18} \ll$$

$$\underbrace{\{4d < 5p < 6s\}}_{\text{dim}=18} \ll \underbrace{\overbrace{\{4f < 5d < 6p < 7s\}}^{n+l=7}}_{\text{dim}=32} \ll \underbrace{\overbrace{\{5f < 6d < 7p < 8s\}}^{n+l=8}}_{\text{dim}=32} \ll \ldots,$$

where the orbitals have been grouped in sets of constant $N = n + l$ (see also Table 2). The dimensions of these sets correspond to a series of repeated 'double squares':[8, 331]

$$2 - 2 - 8 - 8 - 18 - 18 - 32 - 32 - \ldots. \qquad (6)$$

The hydrogenic dimensions appear exactly twice in the Madelung sequence — a phenomenon known as the 'period doubling'.

Table 2: Application of the Madelung rule according to which the orbitals in neutral atoms are filled in order of increasing $n + l$, and n for fixed $n + l$.

$n + l$	$l = 3$	$l = 2$	$l = 1$	$l = 0$	N_{n+l}^{max}	$Z_i \to Z_f$	$X_i \to X_f$
1	—	—	—	$1s^2$	2	$1 \to 2$	H $\to$ He
2	—	—	—	$2s^2$	2	$3 \to 4$	Li $\to$ Be
3	—	—	$2p^6$	$3s^2$	8	$5 \to 12$	B $\to$ Mg
4	—	—	$3p^6$	$4s^2$	8	$13 \to 20$	Al $\to$ Ca
5	—	$3d^{10}$	$4p^6$	$5s^2$	18	$21 \to 38$	Sc $\to$ Sr
6	—	$4d^{10}$	$5p^6$	$6s^2$	18	$39 \to 56$	Y $\to$ Ba
7	$4f^{14}$	$5d^{10}$	$6p^6$	$7s^2$	32	$57 \to 88$	La $\to$ Ra
8	$5f^{14}$	$6d^{10}$	$7p^6$	$8s^2$	32	$89 \to 120$	Ac $\to$ 120

According to Goudsmit and Richards, the Madelung rule 'is remarkably well obeyed throughout the periodic table.'[9, 664] Indeed, both the Madelung rule and the period doubling are considered to be of paramount importance to the periodic system. The Madelung rule flawlessly accounts for the overall structure of the periodic table, by predicting the onset of the different blocks in the periodic table, such as the start of the transition metal block ($3d$-block) after the $4s$-block, or the inset of the lanthanide and actinide series (f-block elements) after the $6s$- and $7s$-elements respectively.

It can also be used as the basis for a novel representation of the periodic law, which is known as the 'eight-period' or 'left-step' periodic table (LSPT). The LSPT was first introduced by the amateur biologist Charles Janet in 1929, and offers a number of advantages as compared to the conventional format of the periodic law. First, the periods in the LSPT are characterized by a constant value of $N = n + l$, which suggests the possibility of elevating N to a new quantum number for the periodic system. Second, the period doubling is clearly highlighted in the LSPT. The pairing of the periods gives

the LSPT its stepped profile, and leads to the set of cardinalities in Eq. (6). Third, the ordering of the blocks, when read from right to left, follows the natural filling of the orbitals (s-p-d-f).

4.2   The Löwdin challenge

Until this day, however, the Madelung rule has remained an *empirical* (or '*lexicographic*') rule. As a result, Allen and Knight have named it a 'somewhat mysterious algorithm'.[10, 83] In 1969, during the centennial anniversary of Mendeleev's discovery, Per-Olov Löwdin published 'Some Comments on the Periodic System of the Elements', and noticed how remarkable it was that 'in axiomatic quantum theory, the simple $(n + l, n)$ energy rule has not yet been derived from first principles' (*i.e.* on the basis of the many-electron Schrödinger equation).[8, 332]

The search for such an *ab initio* derivation of the Madelung rule is now known as the 'Löwdin challenge', and is considerd the 'oldest and largest standing problem in quantum chemistry'.[10, 83] Many claims to a successful derivation have appeared in the scientific literature since Löwdin's plea, but most have been dismissed.[11]

Consequently, both the validity and the utility of the Madelung rule have been called into question in recent years. One of the main voices in this debate is Eugen Schwarz, who deplores the importance that is generally given to the $(n + l, n)$ rule.[12, 13, 14, 15] According to Schwarz, the Löwdin challenge is impossible to meet since the Madelung rule is just an "approximate rule of thumb [. . .] at variance with too many facts."[14, 441] Instead of praising the $n + l$ rule, we should be talking about the '$n + l$ blunder', dixit Schwarz.[12, 3412]

In order to back up this claim, Schwarz does raise a number of important issues which would benefit from closer scrutiny. But in our opinion, Schwarz dismisses the Madelung rule for the wrong reasons, and thereby fails to recognize the crucial role the $(n + l, n)$ rule has to play in the study of the periodic law.
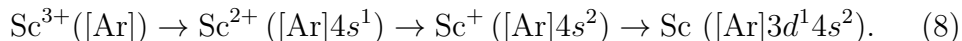
4.3 Interpreting the Madelung rule

Three interpretations of the Madelung rule can be distinguished in the scientific literature. The first two interpretations fail to hold in general — a point made most explicit by Schwarz. For Schwarz, this is sufficient to throw the Madelung rule into the dustbin of chemistry. But he thereby overlooks a possible third interpretation, which does apply universally. When Wheeler embarked on his quest for a 'chemical mechanics', he probably had the second interpretation in mind (see further).
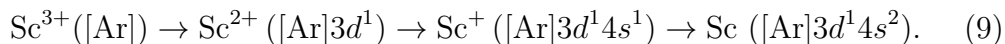
First interpretation. According to the first (and most common) interpretation, the Madelung rule is an Aufbau principle which provides the energy ordering of the different nl states:

$$E(1s) \ll E(2s) < E(2p) \ll E(3s) < E(3p) \ll E(4s) < E(3d) \ll \dots. \quad (7)$$

But this order is erroneously assumed to be fixed and universal. For example, according to the above energy sequence, the Aufbau process of a scandium atom proceeds as follows:

$$\text{Sc}^{3+}([\text{Ar}]) \rightarrow \text{Sc}^{2+}([\text{Ar}]4s^1) \rightarrow \text{Sc}^+([\text{Ar}]4s^2) \rightarrow \text{Sc}([\text{Ar}]3d^14s^2). \quad (8)$$

The $4s$ orbital is thus filled before the $3d$ orbital, as dictated by the Madelung order in Eq. (7). But this is contradicted by the empirical date which shows that configurational reorganizations occur when adding electrons to a bare nucleus. As a result, the $3d$ orbital is initially lower in energy as compared to the $4s$ orbital, and is therefore filled first:

$$\text{Sc}^{3+}([\text{Ar}]) \rightarrow \text{Sc}^{2+}([\text{Ar}]3d^1) \rightarrow \text{Sc}^+([\text{Ar}]3d^14s^1) \rightarrow \text{Sc}([\text{Ar}]3d^14s^2). \quad (9)$$

This refutes the simplistic interpretation of the $(n+l, n)$ rule as a fixed energy ordering principle, which could somehow account for the entire building-up process of atoms from scratch.

Second interpretation. According to the second interpretation, the Madelung rule merely predicts the final electronic configuration of neutral atoms. That

is, the Madelung rule establishes in which nl spin orbital the differentiating electron should go. This clearly holds true for the scandium example above where the predicted Madelung-configuration and the experimentally obtained configuration for a neutral scandium atom are seen to agree.

However, even this weaker interpretation of the Madelung rule does not hold universally. Terry L. Meek and Leland C. Allen [16] have listed 19 elements with anomalous configurations that differ from those predicted by the Madelung rule (Table 3). Having said that, each of these 19 elements also has excited states near the ground state which *do* satisfy the Madelung rule. As a result, it is not clear how much weight should be attached to these exceptions.[2]

Third interpretation. According to the third and final interpretation, the Madelung rule foretells the onset of atomic subshell occupations in the Aufbau sequence of the periodic system. As noted above, it correctly predicts the start of the transition metals, lanthanide and actinide series. It thus accounts for the (at first sight *ad hoc* looking) layout of the different *s*-, *p*-, *d*- and *f*-blocks in Mendeleev's system, and this without exception. In doing so, it moreover discloses the period doubling as another characteristic feature of the periodic table.

4.4   The chemical orbit

In his 1971 contribution, Wheeler adhered to the second interpretation of the empirical Madelung rule, which leads to the conclusion that the energy of the outer electron is governed by the $n + l$ rule:

$$E = n + l = n_r + 2l + 1. \tag{10}$$

Interestingly, Wheeler adds in a footnote a further comment, instigated by a question of the Italian nuclear physicist and Nobel laureate Emilio Segrè.

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[2]Demkov and Ostrovsky [17] have made an interesting and rather telling comparison in this regard between the hydrogenic (n, l) and Madelung $(n + l, n)$ order.

Table 3: Ground state electronic configurations for 19 elements with anomalous configurations that do not follow Madelung's rule. [Data obtained from the National Institute of Standards and Technology (NIST) Atomic Spectra Database. Available online: http://physics.nist.gov/asd]

Element	Predicted Madelung ground state configuration	Experimentally obtained ground state configuration
Cr	[Ar] $3d^44s^2$	[Ar] $3d^54s^1$
Cu	[Ar] $3d^94s^2$	[Ar] $3d^{10}4s^1$
Nb	[Kr] $4d^35s^2$	[Kr] $4d^45s^1$
Mo	[Kr] $4d^45s^2$	[Kr] $4d^55s^1$
Ru	[Kr] $4d^65s^2$	[Kr] $4d^75s^1$
Rh	[Kr] $4d^75s^2$	[Kr] $4d^85s^1$
Pd	[Kr] $4d^85s^2$	[Kr] $4d^{10}$
Ag	[Kr] $4d^95s^2$	[Kr] $4d^{10}5s^1$
La	[Xe] $4f^16s^2$	[Xe] $5d^16s^2$
Ce	[Xe] $4f^26s^2$	[Xe] $4f^15d^16s^2$
Gd	[Xe] $4f^86s^2$	[Xe] $4f^75d^16s^2$
Pt	[Xe] $4f^{14}5d^86s^2$	[Xe] $4f^{14}5d^96s^1$
Au	[Xe] $4f^{14}5d^96s^2$	[Xe] $4f^{14}5d^{10}6s^1$
Ac	[Rn] $5f^17s^2$	[Rn] $6d^17s^2$
Th	[Rn] $5f^27s^2$	[Rn] $6d^27s^2$
Pa	[Rn] $5f^37s^2$	[Rn] $5f^26d^17s^2$
U	[Rn] $5f^47s^2$	[Rn] $5f^36d^17s^2$
Np	[Rn] $5f^57s^2$	[Rn] $5f^46d^17s^2$
Cm	[Rn] $5f^87s^2$	[Rn] $5f^76d^17s^2$

Segrè asked if the formula often employed in spectroscopy for the correlation of atomic energy levels could also lead to this rule. The formula Segrè refers

Table 4: Empirical quantum defect Δ_{nl} for the rubidium atom.

s	p	d	f
3.13	2.64	1.35	0.016

to is the empirical correction to the Rydberg expression for atomic spectra, and goes back to the early days of atomic spectroscopy. A comparison of the energy level diagrams in the alkali series to the hydrogen spectrum shows that the same pattern appears but energies are shifted. It was realized that the single outer electron in the alkali elements is moving about an atomic core, whose field shows marked deviations from the Coulomb field of a point charge. In order to cast the energies of the valence electrons in a Rydberg type formula, it is required to use effective quantum numbers which show a quantum defect with respect to the hydrogenic quantum numbers:

$$n^* = n - \Delta_{nl}. \tag{11}$$

The defect Δ_{nl} represents an empirical expression for the screening of the outer electrons by the core. Observations show that it is nearly independent of n, and is a rapidly decreasing function of l. This is consistent with the dominant role of the angular momentum in the screening properties. As an example, in Table 4 are listed values of Δ_{nl} for the rubidium atom.[18, 19]

By approximating the defect as $\Delta_{nl} \sim a - bl$ the effective quantum number is rewritten as:

$$n^* = n - \Delta_{nl} = 1 - a + n_r + (1 + b)\,l. \tag{12}$$

So for $a = 0$ and $b = 1$ the empirical formula would converge to the Madelung expression.

From the perspective of Bertrand's Theorem two important aspects relate to the kinematic viewpoint of Wheeler. Firstly, since the angular frequency is twice the radial frequency it can be inferred that the orbit of a classical
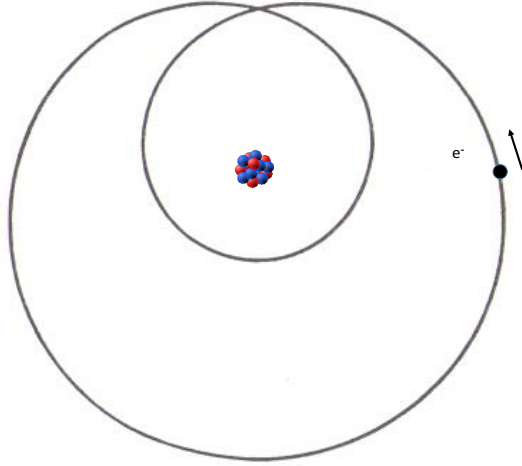
Figure 4: The chemical orbit as a double necklace.

particle in such a modified force field would involve two turns around the
center before reaching the same closest radial distance again. Such an orbit
was termed the 'chemical orbit' or 'double necklace' by Wheeler [2] and his
collaborator Powers [20], as shown in Figure 4. Secondly, since Bertrand's
Theorem does not yield other power laws than the two elliptic cases, it can
be concluded that there is no simple universal force law that would stabilize
classical chemical orbits, irrespective of the initial conditions.

5 Contribution from optics

5.1 Maxwell's fish-eye lens

The direct problem, originating from Wheeler's contribution, is how to infer
a potential that would have the characteristics of the chemical orbit as its
solution. An intriguing answer to this question was proposed by Demkov and
Ostrovsky [21] who came forward with a potential, derived from a century
old problem in optics, published in the *Cambridge and Dublin Mathematical
Journal* in 1853. This journal was founded as the *Cambridge Mathematical
Journal* in 1837 to support the revival of pure mathematics in Victorian

England.[22] Not being patronized by an Academy or Society, its financial situation was often precarious and it heavily relied on the contributions of volunteers. In 1845 it was renamed the *Cambridge and Dublin Mathematical Journal* in an attempt to gain support from Trinity college in Dublin.

In 1853 as a rare instance of interference in editorial matters, the publisher MacMillan suggested to attract more readers by introducing a Problems Page. The solutions would then appear in the next issue. One of these problems was to find a refraction law for a transparent medium such that all the rays proceeding from a given point would meet accurately at another point. The next issue then gave the solution which since then is known as Maxwell's fish-eye lens. The problem and its solution were anonymous, as was quite often the case in those days since "it was the material presented which was important and it was a matter of accepted social form that the author should not draw attention to himself by self-advertisement."[22] Anonymity was not entirely inspired by noble motives though, as it also enabled an attack to be mounted without the wider world being aware of the identity of the attacker.

Only later, when the collected works of Maxwell were published, this problem was included, thus establishing Maxwell's authorship.[23] The solution considered a spherical lens, made of a transparent medium with a gradient index of refraction, provided by the function:

$$n(r) = n(0)\frac{a^2}{a^2 + r^2}. \tag{13}$$

Here $n(0)$ is the value of the refractive index in the center of the sphere. In a note the author explained that the possibility of the existence of a medium of this kind possessing such remarkable optical properties was suggested to him by the contemplation of the structure of the crystalline lens in fishes. The functioning of this lens can be illustrated through the analogy of the propagation of flexural waves in an elastic plate.[24] The desired gradient index profile in the plate was obtained by tuning the thickness. In this way a mechanical analogue of the fish-eye lens could be built. Flexural waves emitted from a point-like pulse on one side of the lens travel through the
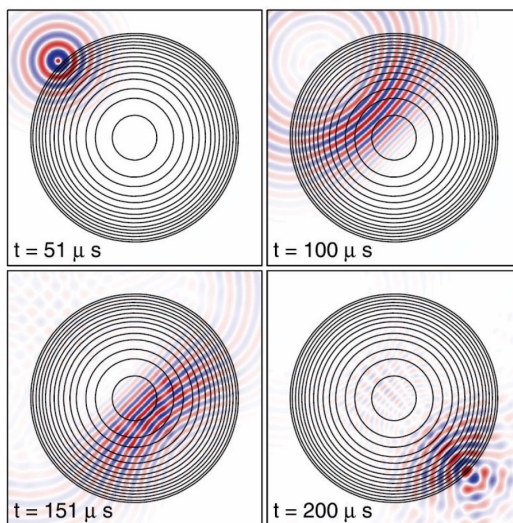
Figure 5: Illustration of the focusing property of a fish-eye lens by the flexural waves in an elastic plate. The contour lines indicate the spatial modulation of the thickness of the plate, corresponding to the refractive index in optics. The source is a Gaussian 60 kHz pulse at the top of the lens. The pulse propagates through the lens and is recovered at the bottom (from Ref. [24]).

medium, and are collimated again at precisely the opposite point on the sphere. Figure 5 presents the results of a simulation which proves to be in close correspondence with the experiments.

Later on Wilhelm Lenz (the same Lenz as in the Runge-Lenz vector) provided a generalization of this refraction law,[25] which was expressed as follows:

$$n(r) = n(0) \frac{\left(\frac{r}{a}\right)^{\mu-1}}{1 + \left(\frac{r}{a}\right)^{2\mu}}. \tag{14}$$

For the index $\mu = 1$ this expression reduces to Maxwell's fish-eye lens, where the image point is exactly opposite the source. For a general value of the index, the image point is obtained at an angle of π/μ, *e.g.* for $\mu = 2$, image points will be found at $\pi/2$, π, and $3\pi/2$. This equation has found important technological applications in the field of optics, but at present we are more

interested in its potential relevance for electronic motions inside the atom. For this we have to cross the bridge that links optics to mechanics.

5.2 The optical-mechanical analogy

In the history of physics, mechanics and optics have always been closely related, finally culminating in Schrödinger's wave mechanics in which the particle and wave nature came together. The optical-mechanical analogy, as expressed by Hamilton, refers to the isomorphism between the trajectories of a particle moving in a potential, and that of a light ray propagating through a medium.[26] It stems from analogous conservation laws and can be expressed as an equivalence between the momentum of a particle and the refraction index of a light ray:

$$p(\mathbf{x}) \Leftrightarrow n(\mathbf{x}). \tag{15}$$

In turn the momentum may be related to a potential energy by:

$$\frac{p^2}{2m} = E - V(\mathbf{x}). \tag{16}$$

Here E is a constant energy. In this way the refractive law for the generalized fish-eye lens may be turned into an attractive potential. A classical particle moving at zero energy is thus expected to describe characteristic orbits that would visit the focal points of the fish-eye lens. By combining Eqs. (14) and (16), with $E = 0$ this potential is easily obtained:

$$V_{\text{eff}}(\mathbf{r}) = -\frac{2v}{r^2 a^2 \left[(r/a)^{-\mu} + (r/a)^{\mu}\right]^2}, \tag{17}$$

with v, μ and a constant parameters. For integer values of μ the trajectory of the particle will resemble a rose window with μ lobes. Hence for one turn it will exhibit μ radial oscillations, corresponding to the quantum rule $\mu\, n_r + l$. From this observation one can also immediately infer that the opposite ratio between radial and angular oscillations can simply be achieved by turning μ into a whole fraction. For $\mu = \frac{1}{2}$ the trajectory will be characterized by half a radial oscillation for one full turn, or one radial oscillation for two angular

oscillations, as required for the chemical orbit. This is the potential proposed by Demkov and Ostrovsky to describe the multi-electronic atom.[21] It should be clear though that this treatment does not yield a universal force law for the Madelung atom, as it does not describe bound states but refers to an isolated solution at zero energy.

6   Conclusion

Ultimately one is facing a paradox that on the one hand the Madelung rule hints at the existence of a universal force law that would regulate the mechanics in a multi-electronic atom, while on the other hand the unbreakable truth of Bertrand's theorem seems to exclude the existence of such a law.

The only escape from contradiction is to rethink the premises for Bertrand's law and the way they reflect on quantum mechanics. Along this vein, in our recent monograph we have explored the possibility of a more general pattern, not from the point of view of potentials, but from the point of view of the Lie algebras.[11] By imposing the Madelung rule in the manifold of bound states of the Coulomb atom we arrived at a non-linear Lie group structure. In essence this group still has the characteristics of the hydrogen $SO(4)$ symmetry, but its structure parameters are no longer constants but functions of the operators representing the quantum numbers n and $l + \frac{1}{2}$. This reflects the generalization of Kepler's law to a structure where n and l quantum numbers are combined.

7   Appendix

Book 1 of the Newton's *Principia* is concerned with the motion of bodies. In proposition 7, corollary 3, Newton addresses the following problem: suppose a particle follows a given orbit, whether acted upon by a force F_C centered at a point C, or a force F_S acting towards a center S. What is then the ratio of the forces F_C and F_S? The text of the corollary is then as follows:

The force by which body P revolves in any orbit around the center of forces C is to the force by which the same body P can revolve in the same orbit and in the same periodic time around any other center of forces S as the solid $CP \times SP^2$ — contained under the distance of the body from the first center of forces C and the square of its distance from the second center of forces S — to the cube of the straight line CG, which is drawn from the first center of forces C to the tangent of the orbit PG and is parallel to the distance SP of the body from the second center of forces. For the forces in this orbit at any point of it are the same as in a circle of the same curvature.[27]

The ratio can thus be written as:

$$\frac{F_C}{F_S} = \frac{CP \times SP^2}{CG^3}. \tag{18}$$

Figure 6A shows the configuration of these points. In proposition 10, Newton then proves that the centripetal force tending to the center C of an elliptic orbit is as the distance, as exemplified by Hooke's law. The next proposition 11 is the famous proposition where Newton identifies the centripetal force towards the focus of an elliptic orbit as the inverse square law. This proposition is followed by a typical "idem aliter" clause, where the same result is proven in yet another way. The importance of this clause is that it really shows the duality between the two force laws considered in Bertrand's theorem.

In Figure 6B, the point P describes an elliptic orbit around the center C according to the force is as distance law. S and H denote the focus points of the ellips. The dashed line represents the tangent to the orbit in P. The lines EC and IH are parallel to the tangent through the center and the focus point respectively. The force F_S that is oriented to the focus S and gives rise to the same orbit, is then related to the force F_C as:

$$\frac{F_C}{F_S} = \frac{CP \times SP^2}{EP^3}. \tag{19}$$

Here we have applied Eq. (18), noting that the distance CG in Figure 6A corresponds to EP in Figure 6B. Since $F_C \sim CP$, one thus has:
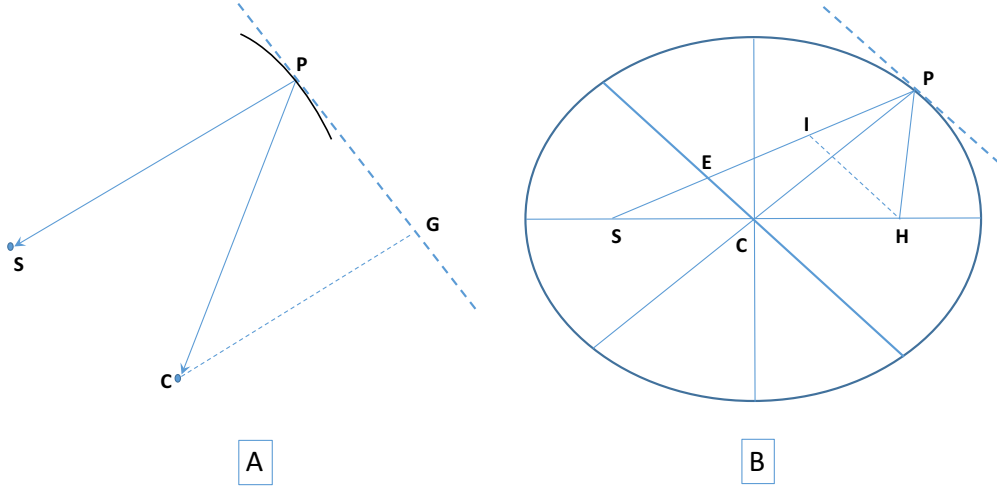
$$F_S \sim \frac{EP^3}{SP^2}. \tag{20}$$

Figure 6: Comparison of attraction force to the center (C) and the focus (S) of an elliptical orbit.

Now, since the triangles ΔSEC and ΔSIH are proportional, one has:

$$
\begin{aligned}
SE & = \frac{SC}{SH} SI = \frac{1}{2} SI \\
& = EI.
\end{aligned}
\tag{21}
$$

Also since the triangle ΔIPH is isosceles, one has:

$$
IP = PH.
\tag{22}
$$

In an ellipse, the length a of the semi-major axis equals the average distance between a point on the ellips and the foci, hence:

$$
a = \frac{SP + PH}{2} = \frac{EP + SE + PH}{2} = \frac{PE + EI + PI}{2} = EP.
\tag{23}
$$

Hence the distance EP is fixed, and thus Eq. (20) reduces to:

$$
F_S \sim \frac{1}{SP^2}.
\tag{24}
$$

Q.E.D.

23

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