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## The Impact of Twentieth-Century Physics on the Periodic Table and Some Remaining Questions in the Twenty-First Century

Eric R. Scerri

#### Abstract

The historical development of the theoretical account of the periodic table provided by theoretical physics is reviewed, beginning with discoveries made at the start of the twentieth century. The article highlights the attempts to theoretically explain several features of the periodic table including the well-known period doubling or Madelung rule of orbital occupation. The account includes more recent group theoretical approaches which go beyond quantum mechanics and seek an explanation based in the underlying symmetry of the periodic table and how this symmetry is broken to produce the diversity of atoms that we are familiar with. The approach taken is one of seeking a global solution to such questions rather than merely solving the equations of quantum mechanics for each individual case.

### 16.1 Early Twentieth Century Developments

The twentieth century began with several influential discoveries that would have a large impact on the development of the periodic table and the study of the elements and that were made over a period of three consecutive years immediately preceding the turn of the twentieth century.<sup>1</sup>

E. R. Scerri (🖂)

<sup>&</sup>lt;sup>1</sup>Although I will use the term periodic table in many cases, the more abstract concept of the periodic system may be more appropriate in some instances. Only in cases having to do with just the representation of the periodic system, is the term "table" entirely appropriate.

Department of Chemistry& Biochemistry, University of California Los Angeles, Los Angeles, CA 90095, USA e-mail: scerri@chem.ucla.edu

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First, Röntgen discovered X-rays in 1895 [1]. In addition to the well-known medical applications of this newly discovered form of electromagnetic radiation, they were soon used to study the structure of crystals and of matter in general. Between 1913 and 1914, Moseley discovered that the frequencies of certain X-ray lines showed a simple relationship with atoms of any particular element [2]. Moseley also succeeded in placing the elements into a more correct sequence that had been available to the discoverers of the periodic system, who had utilized the sequence of increasing atomic weights.

In 1896, just one year after Röntgen discovered X-rays, Becquerel discovered the phenomenon of radioactivity [3, 4] whereby certain unstable atoms decayed, while emitting particles of radiation including  $\alpha$ ,  $\beta$  and  $\gamma$  particles as they were subsequently identified by Rutherford. The very next year, Thomson discovered that the atom was not the featureless sphere that Dalton and others had imagined, because it seemed to contain some smaller particles [5] that were dubbed "electrons" by Stoney. While Thomson believed that these electrons were somehow embedded into the positive charge of the atom, his onetime student Rutherford led a team that fired beams of  $\alpha$  particles at a thin gold foil and found a scattering pattern that could only be explained by assuming the presence of a dense small and positive nucleus at the center of any atom [6].

But even before the birth of Rutherford's nuclear atom, Thomson made one of the first attempts to explain the periodic table on the basis of his own model of the atom [7]. Most textbooks typically focus on the fact that Thomson regarded electrons as being embedded in the atom. These accounts typically fail to mention that Thomson also suggested that electrons were arranged as a series of concentric rings and that analogous arrangements of such rings could explain the similar properties among elements residing in the same groups of the periodic table. The essential physical explanation for the existence of chemical periodicity has therefore been in existence for well over 100 years, even if Thomson was mistaken as to how many electrons the atoms of each element possessed and the manner in which they moved. Among other notable contributors to early atomic theory one must mention the Curies who took up the exploration of Becquerel's radioactivity and succeeded in discovering the two elements of polonium and radium.

Meanwhile, starting in 1900 Planck unwittingly initiated the quantum revolution while explaining the radiation emanating from incandescent bodies such as light bulb filaments [8]. What emerged from his study was the counter-intuitive notion that black-body radiation was emitted only in discrete packets. The first significant application of this concept was made by Einstein, while he was in the process of explaining the photo-electric effect [9]. When light strikes a metal, with a sufficient energy, that depends of the metal in question, electrons are released and gain kinetic energy. This kinetic energy does not depend on the intensity of the light, as one might expect on the understanding that light is a wave phenomenon. Instead, the kinetic energy depends on the frequency of the light, but only if a certain threshold frequency is exceeded. Einstein resolved these apparent anomalies by suggesting

that Planck's energy quantization applied to light in general rather than just black-body radiation. Einstein further postulated the existence of quanta, or particles, of light energy so that one quantum is required to dislodge each single electron before imparting kinetic energy to it.

In 1913 Bohr made another significant application of Planck's old quantum theory when he introduced it to the structure of the hydrogen atom [10]. By means of an ad hoc argument, Bohr asserted that electrons were confined to specific quantum orbits and that they could only undergo transitions to other fixed orbits. In the process of such transitions, as Bohr maintained, electrons could only absorb or emit specific quanta of energy which were reflected in the discrete spectra that had been obtained for any particular atom in the chemist's periodic table.<sup>2</sup>

Moreover, Bohr was able to provide more accurate electronic arrangements (now termed configurations), than Thomson had been able to, since the correct number of electrons in the atoms of all the elements had been deduced by then. As is well known, Bohr's model was extended by Sommerfeld in 1916 by appealing to the special theory of relativity and by assuming that Bohr's orbits were elliptical rather than only circular, thus effectively introducing a second degree of freedom to each electron [11]. This in turn resulted in the need to quote two quantum numbers in order to identify any particular electron, one more than in Bohr's original model with its one quantum number that corresponds to the main shell number.

A completely unknown Cambridge graduate student, Stoner [12], then introduced the use of a third quantum number, quickly followed by Pauli who, in 1925, added yet a fourth degree of freedom and accompanying fourth quantum number for each electron. Pauli announced his Exclusion Principle which would shortly be interpreted to require that the wavefunction of an atom is anti-symmetrical on the interchange of any two electrons [13].

Meanwhile, from 1923, a separate development was taking place in the context of wave-particle duality that Einstein had initiated. De Broglie proposed that wave-particle duality might work in both directions as it were [14]. Just as light waves had been shown to behave as particles, De Broglie proposed that particles, like electrons, might possess an intrinsic wave nature. The experimental confirmation of this proposal was achieved soon afterwards by Davisson and Germer who obtained an interference pattern when they fired a beam of electrons at a small crystal [15].

Schrödinger, working purely theoretically in 1926, proposed a wave mechanical equation to describe the motion of electrons in an atom [16]. Unlike Bohr's ad hoc quantization of angular momentum of electrons, Schrödinger succeeded in deriving quantization and in obtaining a more detailed description of the allowed motion of

<sup>&</sup>lt;sup>2</sup>Although Bohr's theory was only quantitatively successful for one electron or hydrogenic systems, he applied it in a qualitative fashion in order to understand the periodic system and with a considerable degree of success.

electrons. Such motions were subsequently called orbitals, by contrast with Bohr's deterministic orbits. Solving Schrödinger's equation, by applying suitable boundary conditions, results in an infinite number of solutions which are characterized by three quantum numbers. These numbers corresponded to the quantum numbers mentioned above that had been gradually arrived at by Bohr, Sommerfeld and Stoner in more semi-empirical ways. However, Schrödinger's original treatment did not invoke Pauli's fourth quantum number, which to this day is "tagged on" because it is required by the spectral evidence.<sup>3</sup>

One of the most remarkable aspects of Schrödinger's model, when it is augmented thus with a fourth quantum number, is that it gives an almost complete explanation of the periodic table/system in a way that had eluded Thomson and even Bohr. If one combines together the allowed values of the four quantum numbers, in what I will call the Schrödinger-Pauli model, one can rigorously deduce that subsequent electron shells should contain 2, 8, 18 or 32 electrons in perfect agreement with the various possible period lengths that are found in the modern periodic table (Fig. 16.1).<sup>4</sup>

What makes this result even more significant is that it applies to the humble hydrogen atom with its one electron. And yet this approach provides the outline of an explanation of the capacity for each electron shell and for the possible period lengths for all the current 118 elements. I will be returning to this point in due course because it also contains a hint concerning more recent work on the explanation of the periodic table by appeal to the hydrogen atom.

Textbooks frequently rest contented with the Schrödinger-Pauli explanation for the periodic table, although it is clear that it can only be regarded as a stepping stone toward a fuller explanation which is not yet available, even after more than 150 years after the discovery of periodicity. What is still lacking is an equally rigorous, or global, explanation of why the sequence of period lengths in the periodic system is 2, 8, 8, 18, 18, 32, 32 (period doubling), instead of 2, 8, 18 and 32 as might be expected from the Schrödinger-Pauli approach.<sup>5</sup>

The order of filling of orbitals does not involve a strictly sequential filling of each shell but more of a filling in a "diagonal manner." This order is often displayed in a mnemonic shown in Fig. 16.2, and called the Madelung or  $n + \ell$  rule [17].<sup>6</sup> On

<sup>&</sup>lt;sup>3</sup>Dirac's more general theory does predict electron spin and hence a fourth quantum number even if Schrödinger's earlier non-relativistic theory does not.

<sup>&</sup>lt;sup>4</sup>The form of the periodic table best suited to making this point is the 32-column or long form table.

<sup>&</sup>lt;sup>5</sup>To be clear, quantum mechanics can exhaustively calculate the experimentally observed configuration of each atom provided that sufficient flexibility is built into the wavefunction. Consequently, it can reproduce the order of shell filling that agrees with the period doubling and the Madelung rule. What is intended by a "rigorous derivation" here, is one that would represent a global solution for the entire periodic table at once, as it were, without having to carry out calculations for every single atom.

<sup>&</sup>lt;sup>6</sup>The rule appears to have been rediscovered a number of times. It is also found associated with the names of Karapetoff, Janet, Bose, Goudsmit, Klechkowski and Keller, somewhat depending on the national origin of the textbook that one examines. Nevertheless, the Francophone world seems to assign the rule to the Russian physicist Klechkowski.

H 1	]																														He	2
Li	Be	]																								B	ç	N	0	F	Ne	8
Na 11	Mg																									AI 13	Si 14	P 15	8 16	CI 17	Ar 18	8
K 19	Ca															Sc 21	Ti 22	V 23		Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge	As 33	Se 34	Br	Kr 36	18
Rb	Sr 38															Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru	Rh	Pd 46	Ag	Cd	In 49	Sn 50	Sb 51	Te 52	1	Xe 54	18
Cs 55	Ba	La 57	Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	H0 67	Er 68	Tm 69	Yb 70	Lu 71	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg	TI 81	Pb 82	Bi 83	Po 84	At 85	Rn 86	32
Fr 87	Ra 88	Ac 89	Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lr 103	Rf 104	Db 105	Sg 106	Bh 107	Hs 108	Mt 109	Ds 110	Rg 111	Cn 112	Nh 113	FI 114	Mc 115	Lv 116	Ts 117	Og 118	32

Fig. 16.1 32-column periodic table which most clearly displays the variation in period lengths, given by the formula  $2n^2$ 



**Fig. 16.2** Madelung or  $n + \ell$  rule purporting to show order of orbital occupation



**Fig. 16.3** This is how the periodic table would look if shells were to be filled in strict sequence, of only starting a new shell after the previous one is complete, beginning with the innermost shell. The familiar grouping of elements is lost, apart from the elements shown in red, a feature that appears to be coincidental. The fifth period of 50 elements has been truncated for the sake of convenience

the other hand, if the shells were to fill in a strictly sequential manner, meaning that each shell would fill completely before moving onto the next one, the result would be a rather unusual table as shown in Fig. 16.3 which would not reflect the chemical resemblances within groups in the conventional periodic table.<sup>7</sup>

#### 16.2 Developments in the Second Half of the Twentieth Century

The unfortunate fact, for those who claim that the periodic system has been fully reduced, or explained by quantum mechanics, is that the Madelung rule itself has not yet been derived from first principles. This situation was highlighted by the theorist Löwdin while speaking at a conference to mark the 100th anniversary of the periodic table [18]:

The energy rule for the neutral atoms was obviously in contradiction to Bohr's calculation on the hydrogen atom, which indicated that the energies should be increasing with increasing *n*. It is typical of the nature of "frontier-research" that Bohr abandoned this rule for the higher atoms, since it led to the wrong structure of the periodic system, and the modified rule  $[(n + \ell, n)]$  seems to have been obtained in a more intuitive way. Bohr himself was never too explicit about his "Aufbau" principle, and [the rule] is sometimes referred to as the Goudsmit-rule or the Bose-rule. It is perhaps remarkable that, in axiomatic quantum theory, the simple energy rule has not yet been derived from first principles. [p 332]

Although many attempts have been made to explain what is sometimes referred to as the doubling of period lengths (except for the first period), none of them have been successful [19-23].

Moreover, some authors have sought to eliminate the Madelung rule because it fails to provide the precise order of orbital occupation for any particular atom starting with that of scandium [24–27].<sup>8</sup>

Indeed, the  $n + \ell$  rule has little meaning in chemistry. However, since the rule occurs in all textbooks and is absorbed by all students and teachers, it will die out only very slowly. Only a few chemists need correct details about the electronic structure of the chemical transition elements; their re-education in graduate courses is not too difficult. Most other undergraduate students will not need the  $n + \ell$  blunder in their future career. [25]

These claims have been countered by various authors who point out that the Madelung rule remains valid when considering the nature of the differentiating electron, meaning the electron that makes a difference between any particular atom and the subsequent one [28-30].

<sup>&</sup>lt;sup>7</sup>The order of occupation of orbitals in the ions of each atom is a different matter and is not given by the Madelung Rule.

<sup>&</sup>lt;sup>8</sup>The configuration predicted for scandium by the Madelung rule is  $[Ar] 4s^2 3d^1$ . However spectral data shows it to be  $[Ar] 3d^1 4s^2$ . Similar apparent violations of the rule occur for all transition metals and those from the f-block of the periodic table.

Schwarz is correct in saying that the Madelung rule is violated when it comes to the progressive occupation of orbitals in any particular atom. But it is still true that the electron that differentiates an element from the previous one in the table follows Madelung's rule. In the case of potassium and calcium, the "new electron" relative to the previous atom is a 4s electron. But in scandium, the electron that differentiates it from calcium is a 3d one, even though it is not the final electron to enter the atom as it builds up. In other words, the simple approach to using the aufbau principle and the Madelung rule remains valid for the periodic table viewed as a whole. It only breaks down when considering one specific atom and its occupation of orbitals and ionization energies. The challenge of trying to derive the Madelung rule therefore remains, pace Schwarz. [28]

I would now like to turn to one promising line of research which has been in the making for more than 50 years and which brings us back to the hydrogen atom and its potential to generate the entire periodic table.<sup>9</sup> I am referring to the group theoretical approach to explaining the precise lengths of all the periods in the periodic table on the basis of the special symmetry of the hydrogen atom.

#### 16.3 The Special Dynamical Symmetry of the Hydrogen Atom

The energy levels in the hydrogen atom that share a common n quantum number value all have the same energy.<sup>10</sup> This property, that is given the name of degeneracy, is rather difficult to explain fully using quantum mechanics. The first person to do so was Pauli who drew on the dynamical symmetry of the hydrogen atom, as will be explained. It is important to appreciate that this symmetry goes beyond the spherical shape of the electron distribution around the nucleus of the hydrogen atom.

The hydrogen atom features just one electron of course, that experiences a Coulombic force of attraction. This highly symmetrical scenario is responsible for the degeneracy among energy levels that share the same *n* and  $\ell$  quantum numbers. For example, the three 2p orbitals in the hydrogen, and indeed any atom, are known to possess the same energy in the absence of perturbations. However, the hydrogen

<sup>&</sup>lt;sup>9</sup>Cosmologists also consider hydrogen to have been the progenitor of all other elements in the sense that the first element to form after the Big Bang was indeed hydrogen. This can be considered as a modern-day version of Prout's hypothesis whereby all elements were regarded as composites of hydrogen, which of course they are if one focuses on the number of protons in the nucleus of the atom of any particular element.

<sup>&</sup>lt;sup>10</sup>This is no longer the case if one considers the fine structure among spectroscopic levels or the even smaller splitting due to the Lamb shift. The approximate degeneracy being referred to is a feature of the non-relativistic Schrödinger treatment of the hydrogen atom. More strictly speaking, there is already nonrelativistic lifting of degeneracy at the Schrödinger level due to the finite size of nuclei which are not point charges without structure, but spatially extended objects. Further contributions to fine structure also arise from electron spin and the mass of the electron. I am grateful to a reviewer for suggesting this clarification.

atom alone possesses another more remarkable degeneracy, namely the fact that all the orbitals that share the same *n* quantum number have the same energy such as in the case of the 3s, 3p and 3d orbitals in the 3rd main shell. This degeneracy has long been known as an "accidental degeneracy" because its origin was unknown. Nowadays it should no longer be referred to as such since its cause has been fully explained. A full understanding of this issue involves some rather complicated theoretical physics and mathematics and will not be attempted in this article. (Further information on this question can be found in Blinder [31] and Thyssen and Ceulemans [32].) It is important to gather a broad understanding of the question however, because of its importance to recent attempts to obtain a global understanding of the periodic table that involves group theory and that go beyond the use of quantum mechanics in some respects.

As already briefly mentioned, the hydrogen atom possesses additional degeneracy than that associated with its rotational symmetry. This additional symmetry, sometimes described as being a hidden symmetry, is termed "dynamical symmetry" in order to distinguish it from the better-known geometrical symmetry of the spherical potential experienced by the electron.

#### 16.4 The Laplace-Runge-Lenz or LRL Vector

The mathematical key to understanding the degeneracy of the hydrogen atom lies in drawing an analogy to a classical mechanical problem that was analyzed long ago by some well-known mathematicians including, Hermann, Bernoulli, Laplace and Hamilton, each of whom re-discovered a certain vector that has been given various names. Mechanical systems that belong to a class having central forces show a conservation of angular momentum and in addition the conservation of a vector that is known as the Laplace-Runge-Lenz vector since Wolfgang Pauli made use of it in quantum mechanics. The LRL vector is constant in both magnitude and direction at any point during the course of a planet's elliptical motion around the sun, or in the case of the atom, an electron's motion around the nucleus. More specifically, there are three components of the LRL vector which all represent constants of the motion for the planetary system or the classical understanding of the hydrogen atom. The LRL is therefore the key to discovering an extra constant of motion that is associated with the additional dynamical symmetry that exists in the hydrogen atom.

In 1926 Pauli obtained the quantum mechanical version of the LRL vector and was able to explain the formerly known accidental degeneracy of the hydrogen atom. In the same article Pauli used the LRL vector, within Heisenberg's matrix mechanical theory, to obtain the first solution of the energy levels of the hydrogen atom, ahead of Schrödinger's treatment which soon followed [33].<sup>11</sup>

<sup>&</sup>lt;sup>11</sup>The reason why the vector bears the names of Laplace, Runge and Lenz is due to Pauli who learned of the existence of this vector while he was an assistant to Lenz, who in turn referred to the work of Runge and Laplace on the same vector.

Nevertheless, it appears that Pauli lacked the necessary knowledge of group theory that would have enabled him to grasp the full implications of the LRL vector for the question of the symmetry of the hydrogen atom. The latter feat was achieved by the Soviet physicist Vladimir Fock, who is perhaps better known for having modified Hartree's method of approximating the orbitals for many-electron atoms in order to comply with the requirement of the anti-symmetry of the wavefunction in the Hartree-Fock approach to computational chemistry and physics [34].

Returning to the hydrogen atom, in 1935 Fock discovered that the additional degeneracy could be rationalized by appeal to a form of supersymmetry that is hidden within a fourth spatial dimension [35]. Fock's hydrogenic wavefunctions were projections from the familiar three-dimensional space onto the surface of a four-dimensional hypersphere that is technically denoted as a 3-sphere. While the familiar sphere in three dimensions represents the symbol of perfect symmetry, physical phenomena such as the hydrogen atom have led to the realization that there exist symmetries even more perfect in higher dimensional spaces.

Here is how the Mexican group theorist Octavio Novaro explained the situation in a volume consisting of articles presented during the second international conference on the periodic table held in 2003 [36–40].<sup>12</sup>

Let us reflect upon the depth of Fock's achievement: he identified two apparently unrelated systems, the three-dimensional Coulomb potential of the nucleus acting on the electron, and a forceless punctual mass constrained to move on the surface of a hypersphere in four dimensions. He therefore obtained a full group-theoretical explanation of the "accidental degeneracy" of the hydrogen atom. In fact, Fock also provided the closed-shell occupation numbers for model systems consisting of many non-interacting particles captured in an attractive Coulomb potential. These are the so-called "magic numbers" (2, 8, 18, 32, 50 etc.) which in Fock's approach are not or mysterious at all, as they correspond to the irreducible representations of the group O(4)...Elaborating on these results, Bargman demonstrated that the O(4) symmetry of the hydrogen atom stems from the conservation of two constants of motion: the angular momentum in three dimensions and the Runge-Lenz vector and that these are precisely the generators of this group.

This work provided the first significant connection between symmetry principles and attempts to fully explain the periodic table.<sup>13</sup> However, it did not give an explanation of period doubling in the periodic table or the Madelung rule that governs the occupation of atomic orbitals.

<sup>&</sup>lt;sup>12</sup>There have been four international conferences on the periodic table up to the present time. The first was held in the Vatican City to commemorate the centenary of Mendeleev's 1869 article, in which he announced his periodic table, and included presentations from physicists John Wheeler and Emilio Segrè. The second conference took place in Banff, Canada in 2003. The city of Cusco in Peru was the location of the third international conference while the fourth was held in St. Petersburg to commemorate the 150th anniversary of Mendeleev's paper of 1869. Proceedings for all of these meetings have been published [37–40].

<sup>&</sup>lt;sup>13</sup>Novaro's claim that degeneracy was rendered non-accidental as a result of Fock's work is historically inaccurate. As was mentioned above, this development was due to Pauli.

#### 16.5 An Alternative Philosophical Approach of Moving Beyond Particles and Individual Elements: Heisenberg and Isospin<sup>14</sup>

In order to understand the subsequent developments in the still unfolding story, we must go backwards historically and consider the work of another luminary figure among the founders of quantum mechanics, namely Werner Heisenberg. This author was deeply influenced by ancient Greek philosophy and more specifically the writings of Plato. For example, in a book written in 1971 Heisenberg states [41],

The elementary particles in Plato's Timaeus are finally not substance but mathematical forms. [p 8]

and

So far we had always believed in the doctrine of Democritus, which can be summarised by: "In the beginning was the particle." We had assumed that visible matter was composed of smaller units, and that, if only we divided these long enough, we should arrive at the smallest units, which Democritus had called "atoms" and which modern physicists called "elementary particles." But perhaps this entire approach has been mistaken. Perhaps there was no such thing as an indivisible particle. In the beginning was symmetry! [p 133]

Working in the 1930s Heisenberg set out to understand the relationship between the proton and the neutron, two fundamental particles with almost identical masses. These near identical masses implied a degeneracy, which in turn suggested that there might be a form of symmetry that allows for interconversion among these particles. Such transformations are known to occur physically, such as when a neutron is transformed into a proton plus a  $\beta$  particle along with a neutrino [42].

By analogy with electrons which possess two spin states with very similar energies, Heisenberg postulated a property that he termed isospin which characterized the proton and neutron as showing alternative isospin states of the same fundamental particle. While the mathematical symmetry group that allows the spin states of electrons to transform into each other is SU(2), Heisenberg found that the same symmetry group transforms a proton into a neutron and vice versa.

#### 16.6 Gell-Man and the Eight-Fold Way

Heisenberg's approach to the transformation of the proton into the neutron lay dormant for a period of about 30 years before it was revived by the physicist Murray Gell-Mann [43]. By this time the number of elementary particles identified by physicists had greatly increased, so much so that the situation became described as the "particle zoo." This state of affairs was seen to be analogous to the state of chemistry with its sixty or so elements that were recognized before the advent of the periodic table in the 1860s.

<sup>&</sup>lt;sup>14</sup>the remaining parts of the present article draw heavily from the work of Thyssen and Ceulemans [32].



Particle physics began seeking the underlying symmetry which could provide the connection, and indeed the interconversion, of elementary particles within a number of families of particles such as the leptons and hadrons. It was at this point in the development of the field that Gell-Mann found that the SU(3) symmetry group was what was required to bring about transformations among the particles in the hadron family [44].

In addition to providing a fundamental connection between these seemingly distinct particles Gell-Mann's scheme famously allowed him to make a prediction of the existence of a particle that represented a missing gap in his diagram, in much the same way that Mendeleev had left empty spaces and had successfully predicted several new elements when he had tamed the element zoo one hundred years previously in the 1860s. Gell-Mann not only imposed order on the particle zoo, he also successfully predicted the existence of the  $\Omega^-$  that was experimentally confirmed in 1964 [44] (Fig. 16.4).

The success of this approach was rewarded by the Nobel Prize to Gell-Mann in 1969, precisely 100 years after Mendeleev's discovery of the periodic table. This work served to strengthen the philosophical Plato's view that form is more fundamental than substance, and in the terms of Heisenberg, that symmetry is more fundamental than particles. In the latter case, all the members of a family of fundamental particles could be regarded as manifestations of a super-particle whose properties are governed by the underlying symmetry group.<sup>15</sup>

<sup>&</sup>lt;sup>15</sup>The even more recent work on the postulation of the Higgs particle and its experimental verification in the twenty-first century lends further support for the view that symmetry is more fundamental than particles and that the existence of individual particles results from the breaking of symmetry.

Author	Year	Chain of subgroups							
Barut	1972	$SO(4,2) \supset SO(3,2) \supset SO(3) \otimes O(2)$							
Odabaşi	1973, 2010	$SO(4,2) \supset SO(3,2) \supset SO(3) \otimes O(2)$							
Ostrovsky	1980, 1981, 2006	$O(4,2)\otimes SU(2)_{5}\otimes SU(2)_{T} \supset O(4,2)\otimes SU(2)_{5} \supset O(4)\otimes SU(2)_{5} \supset O(3)$							
Novaro and Berrondo	1972	$SU(2) \otimes SU(2) \otimes SU(2) \supset O(4) \supset SO(3)$							
Berrondo and Novaro	1973, 1989, 2006, 2010	$E(4) \supset SU(2) \otimes SU(2) \otimes SU(2) \supset O(4) \supset SO(3)$							
Rumer and Fet	1971	$Spin(4) \supset SU(2)_M, SU(2)_C$							
Konopel'chenko	1972	$SO(2,4) + R \supset SO(2,4) \supset SO(4) \supset SO(3) \supset SO(2)$							
Fet	1974, 1975	$SO(4,2) \otimes SU(2) \supset Spin(4) \otimes SU(2) \supset SU(2)_C \otimes SU(2)$							
Byakov et al.	1976, 1977	$SO(4,2) \otimes SU(2) \supset Spin(4) \otimes SU(2) \supset SU(2)_{\mathbb{C}} \otimes SU(2)$							
Fet	1979, 1980, 1981	$O(4,2) \otimes SU(2) \otimes Z_2$							
Fet	1989, 1992, 1996, 2010	$O(4,2) \otimes SU(2) \otimes SU(2)$							
Kibler and Negadi	1989, 2004, 2006, 2007	$\mathrm{SO}(4,2)\otimes\mathrm{SU}(2)\supset\mathrm{SO}(4)\otimes\mathrm{SU}(2)\supset\mathrm{SO}(3)\otimes\mathrm{SU}(2)\supset\mathrm{SU}(2)$							
Thyssen and Ceulemans	2013	$\mathrm{SO}(4,2)\otimes\mathrm{SU}(2)\supset\mathrm{SO}(3,2)\otimes\mathrm{SU}(2)\supset\mathrm{SO}'(4)\otimes\mathrm{SU}(2)$							

"P. Thysen. "Symmetry and Symmetry Breaking in the Periodic Table: Towards a Group-Theoretical Classification of the Chemical Elements." PhD diss., Katholicke Universiteit Leuven, 2013.

**Fig. 16.5** A table reproduced from Thyssen and Ceulemans [32] showing various ways in which group theorists have examined the breaking of SO(4,2) symmetry in an attempt to explain the period doubling as well as the Madelung rule associated with the periodic table. Reproduced with permission [32]

#### 16.7 Fet, Barut and Others on Super-Elements

In the 1970s, several physicists, working independently, adopted a group theoretical approach to trying to explain the periodic system of the elements in a more fundamental, or global manner, than quantum mechanics had succeeded in doing [45, 46].<sup>16</sup> Authors including Fet in the then Soviet Union and Barut in the US shared the view of Plato, Heisenberg and Gell-Mann that symmetry operates at a more fundamental level than matter or particles [47, 48]. They applied this way of thinking to the periodic table of the elements and postulated the existence of a "super-element" which gives rise to all the individually known elements when symmetry is broken. Just as in the work of Heisenberg and Gell-Mann, it became a question of identifying what symmetry was responsible for the interconversion of any element into any other particular element in this case. Stated otherwise, they sought the particular form of symmetry which when broken could give rise to all the known individual elements.

The required symmetry was identified by various physicists as being SO(4,2). However, there is much disagreement as to how this underlying symmetry should be broken via a series of reductions, to a chain of sub-groups, in order to recover the characteristic period doubling of the periodic table and its associated Madelung rule. As shown in Fig. 16.5, many competing schemes have been proposed. Indeed, there is even disagreement as to whether the Madelung rule requires any explanation at all. Many of these group theoretical approaches are concerned with the super-element as discussed above. Consequently, some of these authors no longer

<sup>&</sup>lt;sup>16</sup>An alternative atomic physics approach was simultaneously explored by other authors including Demkov and Ostrovsky [21], Ostrovsky [45], Novaro [36] and Kibler [46].

feel restricted by having to recover the Madelung rule in particular, which they believe is only relevant when one considers the elements separately as opposed to collectively.

#### 16.8 Conclusion

Attempts to explain the periodic table have been a great driving force for physicists throughout the twentieth century and also into the twenty-first century. Although quantum mechanics provides an ab initio explanation for the lengths of periods, it has not yet explained the phenomenon of period doubling or the Madelung rule which governs the manner in which atoms are built-up as one traverses the periodic table. Beginning in the 1970, but drawing of earlier work stretching back to classical mechanics of a two-body system, group theorists have moved beyond quantum mechanics in order to seek the symmetry that underlies the periodic system. Although considerable progress has been achieved, such as the recognition of the symmetry group that underlies the periodic table, this project has not yet been entirely successful. What remains to be carried out is to discover precisely how the underlying SO(4,2) symmetry is broken to produce the well-known aspects of the table whose earliest version was published by Mendeleev just over 150 years ago.

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