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## HAS THE PERIODIC TABLE BEEN SUCCESSFULLY AXIOMATIZED?

**ABSTRACT.** Although the periodic system of elements is central to the study of chemistry and has been influential in the development of quantum theory and quantum mechanics, its study has been largely neglected in philosophy of science. The present article is a detailed criticism of one notable exception, an attempt by Hettema and Kuipers to axiomatize the periodic table and to discuss the reduction of chemistry in this context.

### 1. HISTORICAL PRELUDE AND THE TREATMENT OF THE PERIODIC SYSTEM AND TABLE IN THE PHILOSOPHICAL LITERATURE

The Periodic Table of the elements has had a profound influence on the development of modern chemistry and physics. In chemistry its influence is well known and undeniable. The periodic system functions as a unifying principle which continues to guide the day-to-day research of chemists in many specialized areas. The influence of the periodic table on the development of physics and in particular quantum mechanics is not so well known but equally undeniable.

Shortly after the turn of the century, J. J. Thomson, the discoverer of the electron, regarded the question of trying to explain the periodic table through atomic physics as one of the major unsolved problems. In 1904 he tried to account for the periodicity of the elements in terms of the arrangement of electrons in rings. Thomson proposed a detailed set of atomic configurations as part of his plumb pudding model in which electrons were embedded in the main body of the atoms and were held to circulate in concentric rings (Thomson, 1904).

The particular arrangement of how many electrons should occur in each ring was adapted from the earlier work of an American physicist Mayer, who had experimented by floating small bar-magnets inside a circular basin of water and observed that stable rings required a particular number of magnets (Mayer, 1878). Although Thomson's tables of electron rings do not show the periodicities at the atomic numbers which we now know them to occur at, it must be remembered that there was still a good deal of confusion as to the numbers of electrons contained by atoms of even low

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atomic weights at this time.<sup>1</sup> Thomson merely showed the plausibility of explaining chemical periodicity by similarities in electronic configurations among atoms of different elements.

Soon afterwards, Thomson's atomic model was deposed in favor of Rutherford's nuclear atom in which the electrons were considered to orbit the small central nucleus. This task was achieved, partly, by Niels Bohr while on his postdoctoral year in Cambridge and Manchester following the completion of a PhD in Copenhagen.

It has been persuasively argued that Bohr was initially concerned with trying to obtain the electronic configurations of the atoms in the periodic table and that only later did his attention turn to the spectrum of hydrogen, for which he seems to be better remembered, especially by physicists (Heilbron and Kuhn, 1969). Indeed, the first time that Bohr introduced the famous condition for the quantization of electron energy it was in the context of examining Thomson's model of electron rings.<sup>2</sup> Bohr was clearly driven by the desire to understand the periodic table of the elements and devoted many articles to postulating electronic configurations for all the known elements as well as elements which had not yet been discovered.

Although Bohr's old quantum theory was initially successful, various technical problems arose including that of the anomalous Zeeman effect which was to exercise the most brilliant physicists of the day. Wolfgang Pauli eventually solved this problem by postulating that electrons possessed a fourth degree of freedom in addition to the three which had been discovered up to that point. Armed with this new quantum number, Pauli then attacked, what he too regarded as a major question, that of the structure of the periodic table. More specifically his motivation was to try to settle the question of the closing of the electron shells, that is to say the varying lengths of successive periods in the table. This was the context in which Pauli discovered the Exclusion Principle which stipulated that no two electrons could share the same four quantum numbers. When this recipe was added to the already established relationship between the previously known three quantum numbers possessed by each electron, the length of successive periods in periodic table emerged in a completely natural manner (Pauli, 1925).

The old quantum theory was eventually found to possess so many problems that it required a major re-formulation on the part of Schrödinger and Heisenberg, whose equivalent but distinct approaches provided a way out of the 'impasse' through quantum mechanics. However, the Pauli principle, regarded as a bridge between the old and the new quantum theories, was retained, albeit in a modified fashion. The reformulation of Pauli's principle called for an abandonment of the notion of stationary states for

individual electrons.<sup>3</sup> Only the atom as a whole could be regarded as possessing stationary states. In the Schrödinger treatment the wavefunction for the system of electrons would be described by a wavefunction which is anti-symmetrical with respect to the interchange of any two electrons, a result which was independently established by Heisenberg and Dirac (Heisenberg, 1925; Dirac, 1926).

In spite of the central role played by the periodic table its importance seems to have been overlooked in the literature on philosophy of science. Indeed there is only a single paper, to the best of the authors knowledge, which is dedicated entirely to the nature of the periodic table (Hetteema, Kuipers, 1988). In addition to this contribution there are a handful of articles in edited collections which deal with certain aspects of the periodic table and periodic law.<sup>4</sup>

However, in view of the interest on the nature of scientific laws in contemporary philosophy of science, (Armstrong, 1988; Dretske, 1977; Lang, 1993; Tooley, 1977; Woodward, 1992), it is somewhat surprising that no major study<sup>5</sup> has been conducted on the law-likeness or otherwise of the so-called periodic law which is embodied in the periodic table.

## 2. HETTEMA AND KUIPERS' ATTEMPT TO AXIOMATIZE THE PERIODIC TABLE

As mentioned above, there has been one single work entirely dedicated to the nature of the periodic table. Kuipers and Hetteema have attempted to obtain an axiomatization of the periodic system and in the process, claim to have answered the question of whether chemistry is reduced to atomic theory.

I will return to the question of axiomatization and reduction later in this paper, but first I examine a number of statements and claims made by these authors in their introduction. [my numbering];<sup>6</sup>

1. "We obtain a naive and a sophisticated version of the Periodic Law and hence of the Periodic Table" (p. 387)
2. "It is claimed [meaning the authors claim] that the physicist and the chemist have a different conception of the atom, that the original version of the Periodic Table is based on the chemist's conception, and that the conception of the physicist, based on the Atomic Theory, has gradually taken its place". (p. 387)
3. "... Atomic Theory can explain (and even reduce) the chemist's formulation of the sophisticated Periodic Law". (p. 387)

4. "... we discuss ... whether the Periodic Table is a proper theory or merely an empirical law". (p. 390)

Claim 1 is based on the notion that the periodic table began as a law of octaves, in other words it was first believed that the repetition in the properties of the chemical elements would occur after an interval of eight elements. This view is attributed by the authors to Mendeleev, the Russian chemist who is generally credited with the discovery of the Periodic Law.

According to Mendeleev, there is a unique periodicity, namely 8 (if we include the inert gases): the 8th element, according to the mass-sequence, before or after a given one is similar to that given one. In terms of atomic numbers Mendeleev's Periodic Law, to be called the naive Periodic Law (NPL), can be formulated as follows

NPL  $e \sim e'$  iff  $|z(e) - z(e')|$  is a multiple of 8.<sup>7</sup> (p. 396)

In fact, at no point in the evolution of Mendeleev's periodic tables, over half of which were published,<sup>8</sup> did Mendeleev ever adopt such a view (van Spronsen, 1969). If one considers the group of alkali metals, for example, and one asks the question of how many elements occur before the repetition of another alkali metal, Mendeleev's most frequently quoted periodic table of 1871 shows a sequence of 7, 7, 17 and 17 . . . . If one includes the noble gases then Mendeleev's tables would give intervals of 8, 8, 18, 18 . . . .<sup>9</sup>

Quite apart from any historical inaccuracy, this is a serious error on the part of the authors since they make this feature, of strict octaves as opposed to varying periodicity, the all-important distinction between what they call the naive and the sophisticated version of the Periodic Table.<sup>10</sup>

SPL . . . [sophisticated Periodic Law] states and hence predicts that similarity implies that the respective atomic numbers differ some instance of  $2n^2$  (2, 8, 18, 32 . . . ) . . . (p. 397)

A similar claim is made in the following paragraph,

SPL . . . states and hence predicts that there is always a similar element at a distance of some instance  $2n^2$  after/before a given element if there is a similar one after/before at all. (p. 397)

These claims on the length of the varying periodicities are also incorrect. The repetition of the elements follows the sequence 2, 8, 8, 18, 18, 32 . . . as opposed to the authors statement that it is 2, 8, 18, 32. The formula of  $2n^2$  which is cited by Hettema and Kuipers refers to the maximum number of electrons which successive shells can accommodate. However, the sequence in which electron shells are filled is complicated by the fact that not all shells are filled completely before a new shell is begun (Löwdin, 1969).<sup>11</sup> This feature, which is ignored by the formula which Hettema and

Kuipers appeal to, gives rise to the transition and inner transition series of elements and hence the characteristic form of the modern periodic table.

This false distinction made by Hettema and Kuipers is one of several, as will be argued, which serve to cause confusion regarding the claims which they make following their axiomatization of the Periodic Table. If there is any sense in which one may distinguish between a naive and a sophisticated version of the periodic table, it lies with the use of atomic weight and later the property of atomic number to order the elements. Whereas atomic weight was first used by the likes of Mendeleev, Newlands and all other pioneers of the periodic table, the subsequent and more fundamental ordering principle is based upon atomic number or number of protons in any atom, following the work of Moseley (Moseley, 1913). Although Hettema and Kuipers show that they are aware of this transition they do not seem to attribute the appropriate significance to it.

In claim 2 the authors express the view that physicists and chemists have a different conception of the atom. It is not clear whether they intend this as a historical claim, which would be correct at a certain epoch of the development of chemistry and physics, or whether they imply, incorrectly, that this is the current view. Later in paper it becomes clear that they do in fact intend this distinction to hold for contemporary chemistry and physics.<sup>12</sup>

In claim 3 it is not clear what Hettema and Kuipers take to be “atomic theory”. Do they take it to mean the ordering of the table according to atomic number instead of atomic weight? Do they take it to mean Thomson’s atomic theory which, as mentioned in the introduction, represented an early attempt to ‘reduce’ the periodic table? Do they intend atomic theory to be identified with Bohr’s theory which provided a deeper explanation of the Periodic Table? Finally, and this is surely the sense which should be attached to the phrase ‘atomic theory’, are the authors referring to the new quantum mechanics of Heisenberg and Schrödinger?<sup>13</sup> When the question of the reduction of chemistry is discussed by philosophers it is usually whether chemistry is reduced to this more mature theory of quantum mechanics (Primas, 1983; Liegener, Del Re, 1987; Scerri, 1994a).

Turning to claim 4, the authors ask whether the periodic table is a proper theory or merely an empirical law. I believe that this statement represents a category mistake. The periodic table itself is neither a theory nor a law. There is no such thing as *the* periodic table. The mere fact that over 700 periodic tables have been produced shows that the representation of the periodic law is rather arbitrary (Mazurs, 1974). What is important is the statement of the periodic law which any periodic table attempts to

represent graphically. I delay a discussion of the main substance of this claim regarding the status of the periodic law.

The following section Hettema and Kuiper's article consists of a brief and generally accurate account of the early historical development of the periodic table. The only important omission would seem to be the author's failure to mention the experimental work of Henry Moseley, in 1913, which established that the correct ordering principle for the elements consists in atomic number instead of a atomic weight. This development is crucial for the arguments contained in Hettema and Kuipers' article, since they go on to discuss whether the ordering number  $z$  (implicit in the work of Mendeleev but explicit in the modern table) is or is not a theoretical quantity. In the course of this discussion the authors suggest that the change in the ordering principle from atomic weight to atomic number is somehow not accessible to experiments.<sup>14</sup>

Moseley initially conducted his experiments on twelve elements, ten of which occupied consecutive places in the periodic table. He thus discovered that a plot of the frequency of the so-called  $K$  lines in the spectrum of each element was directly proportional to the square of an integer representing the position of each element in the periodic table. This result suggested that there is a fundamental quantity in the atom which increases by regular steps as we pass from one element to the next. This quantity was subsequently referred to as the atomic number of an element and eventually identified with the number of protons contained in the nucleus of any particular atom. Moseley's discovery shows unambiguously, that tellurium should be placed before iodine in the periodic table, which is in keeping with the chemical behavior of these elements. The atomic weight ordering which holds that iodine should be placed before tellurium is thereby refuted, as it is in the case of the other pair reversals in the periodic table.<sup>15</sup>

In section 3 Hettema and Kuipers begin their main task of axiomatizing the periodic table. In order to construct a "potential model" for the periodic table the authors depart from the historical development, as one might rightly expect in any attempted axiomatization. The potential model which is to serve to axiomatize the early periodic table as well as the modern version includes both atomic weight and an atomic number function,  $z$ . To justify such an approach the authors state that Mendeleev implicitly realized the need to use  $z$ ,

Mendeleev did not explicitly introduce atomic numbers, but in developing the two-dimensional table, starting from the atomic mass sequence, he left open spaces for not yet discovered elements, just on the basis of his idea that there is a period of 8 elements. Of course in this way he introduced implicitly the atomic numbers. (p. 396)

Whether Mendeleev did implicitly introduce atomic numbers is debatable. It would seem that the above statement rests on the false assumption that Mendeleev was in favor of a constant periodicity of eight elements.<sup>16</sup>

After stating the definition for a potential model the authors explain how their terms  $m$  and  $\sim$  can be determined experimentally and that  $z$  is the only “theoretical term” of the five terms discussed. Now admittedly Mendeleev could not determine  $z$  experimentally and so for him it would indeed have been a theoretical term. However, for the modern periodic table  $z$  is no longer merely theoretical, since it can be measured via Moseley’s experiment, a fact which pre-dates the important developments in atomic theory of Bohr, Pauli, Schrödinger and so on. For the periodic table “based on atomic theory”, as the authors would have it, it must be concluded, contrary to Hetteema and Kuipers, that  $z$  is not in fact a theoretical term.

On page 395 the authors take up their claim to discussing two versions of the periodic table as mentioned in the introduction. Once again, they claim that the latter was developed “in contact with atomic theory”. As mentioned above, if there is any sense in which one can distinguish between a naive and sophisticated form of the table it would be to call Moseley’s version sophisticated. All subsequent developments in atomic theory merely serve to represent, in the sense of presenting again, the periodic table in terms of atomic structure but fail to bring to it any fundamental changes as has been argued elsewhere (Scerri, 1994b).

Another distinction made by Hetteema and Kuipers consists in the difference between what they term the chemical atom and the physical atom. However, the way in which they choose to draw such a distinction is somewhat vague.

In chemistry nowadays there exists a tendency to base qualitative discussions on a highly approximate level of the physical picture of the atom. (In fact, the level of approximation can become so high, that this kind of picture cannot be called ‘physical’ any longer.) (p. 400)

Are the authors perhaps referring to the electronic configurations of atoms at this point? If so, it is not clear at what point this model can be said to cease to be physical as they suggest. After all, atomic physicists make ample use of electronic configurations of atoms, as do chemists.

Hetteema and Kuipers further claim that the

... obtained results, as they emerge out of these qualitative discussions concern mainly molecular properties. (p. 400)

In fact one of the main purposes in using electronic configurations lies in the calculation of ground state energies, a feature which applies equally well

to atoms as it does to molecules. Indeed, the basis sets used in molecular calculations depend on the prior calculation of atomic basis sets. The authors then attempt a more precise explanation of the difference between the chemical and the physical atom and in doing so commit another fallacy.

... a 'chemical' conception distinguishes itself from the 'physical' picture by being primarily meant to describe the role atoms play in molecules. (p. 401)

Unfortunately this interpretation does not leave room for a discussion of the chemistry of atoms or in other words for the attempt to reduce the periodic table of the elements to quantum mechanics<sup>17</sup> or atomic theory, which is a question that Hetteema and Kuipers claim to discuss in their article. The authors continue by saying,

... In the 'chemical' picture of the atom for instance, 'chemical similarity' includes 'having the same valency' while in the 'physical' picture, 'chemical similarity' can be related to similarities in the 'outer electron configuration' (This means automatically that also the concept of 'valency' itself can be related to 'outer electron configuration'.) (p. 401)

In fact the concept of electronic configuration as a causally explanatory feature has become very much the domain of chemistry or to be more precise it is *the* dominant paradigm in modern chemistry. Conversely, physicists are only too aware of the limitations of the electronic configuration model and they only draw upon it as a zero order approximation. Hetteema and Kuipers further state that Bohr's theory of the atom, despite its level of approximation, is to be regarded as a physical theory because the explanation of the periodic table was only a spin-off from its development. But given Heilbron and Kuhn's detailed version of the historical development, it was precisely the explanation of the periodic table which provided the initial impetus for Bohr's famous theory of the atom, whereas the explanation of the hydrogen spectrum only arose later. (Heilbron and Kuhn, 1969).

According to Hetteema and Kuipers,

... the relation  $\sim$  now indicates [in the sophisticated periodic table] the relation of having the same 'valence electron configuration', this means that two elements stand in the relation  $\sim$  e.g., when both have a  $d^3$  configuration. All groups, occurring in the Periodic Table, can be identified with some sort of 'outer electron configuration'. (p. 402)

This statement is factually incorrect. The possession of a particular outer electron configuration is neither a necessary nor sufficient condition for membership of any particular group in the periodic table. To make matters even worse, the example of a  $d^3$  configuration given by Hetteema and Kuipers is rather unfortunate since of the three elements vanadium, niobium



and tantalum which belong to group 15 of the periodic table,<sup>18</sup> by virtue of their very similar chemical properties, only vanadium and tantalum have an electronic configuration which includes  $d^3$ .<sup>19</sup> This example among many others<sup>20</sup> shows that the possession of a particular electronic configuration is not a necessary condition for the display of any characteristic chemical behavior. Similarly, examples may be cited to show that the possession of a particular configuration is not sufficient for the possession of a particular chemical property. The elements helium, beryllium and magnesium, for example, all share an outer shell configuration of  $s^2$  and yet helium is a highly inert gas which is invariably placed at the head of the noble gases while beryllium and magnesium are reactive metals which belong in the alkaline earth group of the periodic table.

In a section entitled "A case of reduction", the authors conclude that the sophisticated periodic table can be explained using atomic theory. The basis for this conclusion is the authors view that the term  $z$  can be identified with the number of electrons in any neutral atom. They state that,

The necessary link between chemical similarity and equal outer electron configuration states that the latter causes the former. (p. 403)

It is interesting to contrast the above statement with that of one of the leading authorities on electronic configurations of atoms,

No simple relation exists between the electron configuration of the ground state of the atom and the chemistry of the element under consideration. (Jørgensen, 1973).

Moreover, a reduction of chemistry, or more specifically the periodic table, to quantum mechanics requires far more than a mere approximate explanation of the properties of elements in terms of outer electron configurations. After all, quantum mechanics or "atomic theory", which the authors constantly allude to, is not a qualitative theory dealing in outer-shell electrons. Such explanations are indeed frowned upon by physicists as being of a typically picturesque and naively realistic kind, typical of chemists. Worse still, according to quantum mechanics, the very notion of electron shells or electron configurations becomes strictly invalid as mentioned in the introduction.<sup>21</sup>

Nevertheless, the connection between chemical behavior and electronic configurations can be improved by approaches practiced in computational quantum chemistry. Calculations generally consist in expanding the wavefunction of a many-electron atom, for example, as a linear combination of terms representing excited state configurations, in addition to the ground state configuration. A more realistic approximation to chemical behavior of atoms is thus achieved through a superposition of numerous, often

thousands, of configurations and not merely the ground state configuration which features exclusively in the qualitative explanation of the periodic system.

Finally, on the basis of their axiomatization, Hettema and Kuipers make the interesting proposal that whereas the periodic table represents a proper theory for Mendeleev, it is an empirical law from the perspective of atomic theory. Although this overall conclusion is partly correct, I believe that the authors arrive at it for the wrong reason. The notion that the periodic table has been reduced by the understanding provided by quantum mechanics is one that is generally held. Of course the degree to which the periodic table has been reduced can be disputed, but most authors favor the view that an approximate reduction of the table has indeed been achieved.<sup>22</sup>

For example, the calculation of the total energy of each atom, a property which shows marked periodicity has been achieved to within  $10^{-3}$  of one percent for many atoms. The situation is somewhat more complicated in the case of atoms with large atomic numbers due to the increasing importance of relativistic effects (Pykkö, 1978).

The point is, that it does not require an axiomatization of the periodic table to reach this conclusion. Indeed, one cannot help thinking that the axiomatization of Hettema and Kuipers serves to accommodate this generally held belief that the periodic table, or more generally chemistry, can be approximately reduced to quantum mechanics. As is frequently the case with any accommodation of already known facts, there remains the suspicion that the theoretical scheme may have been designed with the end in view, perhaps inadvertently. The claimed axiomatization does not predict anything new about the periodic table which is not already known. Furthermore, the promise of precision which such a formal approach could offer, in principle, is lost because of a compensating imprecision in specifying what is intended by the term “atomic theory”. The conclusion that the modern periodic table is not a theory is, likewise, not a new finding. As the authors themselves state, “most books on the subject of practical chemistry” do not treat the periodic table as a theory. Similarly, the philosopher Shapere has taken the view that the periodic table is not a theory but an ‘ordered domain’ despite the excellent predictive power which it provides.

I now turn to the question of a “proper theory” which Hettema and Kuipers have formalized. The gist of their argument is that proper theories have proper theoretical terms whereas an empirical law lacks such terms.

Our claim is that  $z$  is a proper theoretical function in NPT [Naive Periodic Table] and hence that NPT is a proper theory. (p. 405)

However, SPL, and hence SPT, were formulated along with the development of AT [atomic

theory], where the atomic number function  $z$  obtained the interpretation of the number of electrons.<sup>23</sup> (p. 406)

With some plausible definitions we have arrived at the conclusion that it was a proper theory for Mendeleev, and that (the sophisticated version of) the Table became only an empirical law due to the Atomic Theory. (p. 406)

What is clear however is that the Periodic Table is a nice example of a theory which starts as a proper theory which turns at least *de jure* into an empirical law by underpinning it with another . . . (p. 407)

Had Hetteema and Kuipers investigated the status of the early periodic tables of Mendeleev and others they would have discovered that at no time has the periodic table ever been regarded as a theory. This point is relevant, even within the authors framework, given that Hetteema and Kuipers do not seem averse to considering scientific practice in deciding whether the current table is a theory or not.

Furthermore, the mere presence of a single implicit theoretical term within the periodic law does not appear to provide sufficient grounds for the claim that the naive periodic law should be regarded in hindsight as a theory. The periodic systems, both naive and sophisticated, are systems of classification which are devoid of theoretical status in much the same way as the Linnean system of biological classification or the Dewey decimal system of library classification. None of these systems can be regarded as theories since they do not seek to explain the facts but merely to classify them. However, the fact that the periodic system, even in its early stages, was capable of predicting unknown elements such as germanium, in addition to accommodating the properties of all the known elements, suggests that it constitutes a more natural system of classification than systems used to classify library books for example.

Finally, it should be pointed out that any discussion of reducing the periodic table to electronic configurations falls somewhat short of the mark, since the aim should be to reduce electronic configurations themselves to quantum mechanics. However, as Rouvray among others have recently emphasized, electronic configurations are not reduced to quantum mechanics nor can they be derived from any other theoretical approach. They are obtained instead by a mixture of spectroscopic observations and semi-empirical methods like Bohr's aufbau scheme (Rouvray, 1996; Scerri, 1994b; Scerri, 1997).

To conclude, I believe that the periodic table of elements has yet to be axiomatized successfully, although the bold attempt by Hetteema and Kuipers has raised a number of key issues in the philosophy of chemistry.

## NOTES

<sup>1</sup> For example, Thomson believed that the atom of oxygen should contain sixty-five electrons rather than the currently accepted value of eight.

<sup>2</sup> The issue is treated in detail by Heilbron and Kuhn and will not be rehearsed here. See especially pp. 245–248 of their 1969 article. The confusion regarding the supposed primacy of the work on the spectrum of hydrogen stems partly from the order of presentation in Bohr's famous 'trilogy' paper of 1913. Section I deals with the hydrogen spectrum, while sections II and III deal respectively with understanding periodicity through electronic configurations and the structure of molecules.

<sup>3</sup> This result has profound implications for the analysis given in later sections of the present article.

<sup>4</sup> Shapere, 1974; Christie, 1994.

<sup>5</sup> Both articles mentioned in note 4 touch on this question.

<sup>6</sup> In their introduction the authors also say,

For the purposes of easy consultation we include here an example of the Periodic Table. We have chosen for the table in Holton (1973). It is not very modern but for this reason it will look familiar not only to chemists but also to readers with only elementary knowledge of chemistry. (p. 390)

In fact, their choice is not only a very unusual version of the table but would definitely not be the version "most familiar to chemists or those with only an elementary knowledge of the subject" as the authors state. For professional chemists, students of chemistry and casual observers alike, the most familiar form of the periodic table, by far, is the medium-long form which has been in standard use since the 1950's and which the authors repeatedly refer to as the sophisticated version of the table, by which they mean that it embodies the increasing length of periods with atomic number. Mendeleev himself produced a table which is essentially equivalent to the medium-long form as early as 1879. See van Spronsen, 1969, p. 138 for discussion. The modern form of the medium-long table dates from 1905 when it was introduced by A. Werner. (see van Spronsen, p. 152).

<sup>7</sup> Hettema and Kuipers define  $\sim$  as a binary chemical similarity relationship, while  $e$  and  $e'$  are any two elements which stand in such a relationship.  $z$  serves to order the elements according to atomic weight.

<sup>8</sup> Mendeleev produced a total of about thirty different periodic tables in the course of his life.

<sup>9</sup> Mendeleev's earlier table of 1869 gives a sequence of 7, 7, 19, 19 . . . or 8, 8, 20, 20 . . . if the noble gases were to be included.

<sup>10</sup> The naive notion that a repetition of the elements should consistently occur after eight places is due to the British chemist Newlands, who is indeed generally credited with this discovery, as the authors themselves state in a different context.

<sup>11</sup> The order of filling is even more irregular than that suggested by this sequence. There exist about twenty exceptions to the simple aufbau scheme proposed by Bohr. This is one genuine sense in which the periodic table has not been reduced to quantum mechanics or atomic theory. Nevertheless, some recent group theoretical work has explained the sequence of 2, 8, 8, 18, 18 etc. in the order of filling of electron shells but not the anomalies mentioned above. (Kibler and Odabasi, 1973; Novaro, 1973; Kibler, 1989).

<sup>12</sup> Discussion of this point is resumed later in the present article.

<sup>13</sup> Quantum mechanics permitted successful calculations to be made on the energies of atoms other than hydrogenic ones.

<sup>14</sup> The authors quote a paper, by a philosopher, which seems to be the germ of this incorrect notion (Sundaram, 1985).

Even if we say there is an important shift from weight to number one would be hard put to find the crucial experiments to refute or corroborate the old and new 'programs'. (Sundaram, 1985, pp. 111–112)

In fact the experiments performed by Moseley serve precisely this function of falsifying the ordering principle based on atomic weight. Moreover, Sundaram is by no means an authority on the periodic table but one of a few philosophers to have touched on the subject in the literature in philosophy of science. Hettema and Kuipers fail to cite the main authorities on the periodic table such as van Spronsen.

<sup>15</sup> Other pair reversals involve cobalt ( $Z = 27$ ) and nickel ( $Z = 28$ ) as well as argon ( $Z = 18$ ) and potassium ( $Z = 19$ ). The correct symbol for atomic number, or capital  $Z$ , has been used here instead of  $z$  as the authors use throughout their article.

<sup>16</sup> The implicit introduction of atomic number should properly be attributed to Newlands who indeed went further than Mendeleev in giving the elements successive whole number labels based on their atomic weight ordering. Indeed he is the only one of the six acknowledged pioneers of the periodic system to have made this anticipation of the concept of atomic number.

<sup>17</sup> I am referring to such examples as the classification of spectroscopic states or the calculation of ground state energies, both of which properties show marked periodicities.

<sup>18</sup> With reference to the system of labeling groups from 1–18 as introduced by the International Union of Pure and Applied Chemistry (IUPAC).

<sup>19</sup> The outer-shell configurations of these three elements are, vanadium,  $3d^3 4s^2$ ; niobium,  $4d^4 5s^1$ ; tantalum,  $5d^3 6s^2$ .

<sup>20</sup> An even more marked example is shown by the three elements nickel, palladium and platinum each of which shows a different outer sub-shell configuration and yet all three elements are grouped together due to their marked close chemical analogies. The configurations are, Ni,  $3d^8 4s^2$ ; Pd,  $4d^{10} 5s^1$ ; Pt,  $5d^9 6s^1$ .

<sup>21</sup> Indeed, strictly speaking, quantum mechanics forbids any talk of electrons in orbitals and hence electronic configurations (Scerri, 1991).

<sup>22</sup> The reduction is incomplete due to the failure to solve the many-electron Schrödinger equation, a point which will not be labored here. (Scerri, 1994a).

<sup>23</sup> The repeated identification by Hettema and Kuipers of  $z$  with the total number of electrons is incorrect.  $z$  should at all times be identified with the number of protons as is frequently emphasized in elementary courses in chemistry.

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