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ON THE FORMALIZATION OF THE PERIODIC TABLE

ABSTRACT. A critique is given of the attempt by Hettema and Kuipers to formalize the periodic table. In particular I dispute their notions of identifying a naïve periodic table with tables having a constant periodicity of eight elements and their views on the different conceptions of the atom by chemists and physicists. The views of Hettema and Kuipers on the reduction of the periodic system to atomic physics are also considered critically.

1. Introduction

In 1988 Theo Kuipers and a young colleague, Hinne Hettema published an article in which they claimed to have formalized the periodic system of the chemical elements and to have arrived at some conclusions regarding the reduction of the periodic system (Hettema and Kuipers 1988). In 1997 I published an extensive critique of this article in which I claimed that the formalization had been carried out inappropriately and that any subsequent conclusions concerning the reduction of the periodic system by these authors were unfounded (Scerri 1997a).

A few of my criticisms have been addressed by Kuipers and Hettema in their more recent article (Hettema and Kuipers 2000). In addition I have been kindly invited to contribute to the Kuipers volume in view of my earlier critique. What I hope to do in the present article is to put my objections in a clearer manner than I had before. In addition I will attempt to respond to what the authors have said in their initial responses to me in their more recent publication. I believe I now understand the intentions of Hettema and Kuipers more clearly than I did originally and can therefore make my critique altogether more pertinent.

2. Critique of the New Article of 2000

In order to consider the new article I will proceed systematically through its text and will pause to make comments whenever I consider that they are

warranted. Just as they did in their 1988 article the authors are claiming to have carried out a formalization of the periodic system of the elements. More specifically they claim to have obtained a structuralist reconstruction of the development of the periodic system which allows them to discuss the question of the theoretical status of the periodic system. Among the most important issues addressed is "whether the Periodic Table is a proper theory or merely an empirical law." Mendeleev's periodic table and the modern version of the table are referred to as the naïve and sophisticated versions of the table respectively. The difference between them is explored in detail since the authors believe these differences to be "crucial" to their further discussion.

First of all whereas in their original article the authors cited some rather obscure sources on the history of the periodic system, I was gratified to see some attempt to redress the balance which I pointed out was lacking. The more recent article cites the book by Brock. Although this represents an improvement, Brock's excellent overview of the history of the whole of chemistry is not sufficiently comprehensive to be considered as an authoritative treatment of the periodic system. In spite of my earlier suggestion the authors have failed to consult or cite the only existing authoritative book-length treatment of the history of the periodic system by their fellow countryman Johan van Spronsen.

In their introductory section the authors state that one of their main aims is to discuss whether the Periodic table is a proper theory or an empirical law. As I indicated in my earlier comments I fail to see why this question should even arise since as far as I am aware, nobody has ever considered the periodic table as any kind of theory. The periodic table is a mere representation of what is frequently referred to as the periodic law. Whereas the principal discoverer of the periodic system consistently referred to the "periodic law" it is fair to say that modern treatments show less inclination to accord it a law-like status due to the presumed reduction of this law by quantum mechanics. Be that as it may there has never been any question, either at the time when the periodic system originated or in modern times, of regarding the periodic system as any form of theory.

Another issue that is announced in the introduction is that the authors intend to maintain their previously drawn distinction between what they term the naïve periodic law and the sophisticated periodic law. While agreeing that there may be grounds for making such a distinction I disagreed with the way in which the authors sought to make this distinction in my first critique. Since this is one of the points on which the authors seem to have addressed my remarks I will enter into some details and try to take the debate a little further.

According to Hettema and Kuipers the important feature which distinguishes the original periodic tables of Mendeleev and others from the

modern periodic law is that the older versions called for a periodicity of eight elements while the modern form recognizes the fact that the lengths of successive periods can vary. In my first critique I pointed out that Mendeleev had devised many periodic tables and that few of these required that the periodicity of eight be maintained throughout the periodic system. I pointed out that Mendeleev's famous table of 1871 showed periodicities of 7,7,17,17. Hettema and Kuipers now respond by saying that they have consulted the book by Posin and that they have found that there are many different periodic tables. But they still seem to want to focus on one particular periodic table authored by Mendeleev in 1871 which does indeed show a regular periodicity of eight. They also deny my statement regarding the variation of periodicity that I attributed to Mendeleev and for the same year. This confusion is partly my fault since I should perhaps have stated that there were more than one table published by Mendeleev in the year 1871. However by referring the authors to the book by Van Spronsen I had hoped that they would discover this fact for themselves. Instead they have concentrated their attention on yet another marginal source, as far as serious scholarship on the periodic system is concerned, and they seem to have formed the opinion that there was only one Mendeleev table of 1871.[1]

As I also pointed out, Mendeleev's very famous first published table of 1869 does not show the elements distributed into periods of eight.[2] Indeed even in the cases where Mendeleev appears to be implying a periodicity of eight, if one looks at his table closely one notices that some of the columns consist of two columns of elements offset from each other. To maintain the notion of a periodicity of eight one would need to consider all such elements within a column as chemically analogous. Mendeleev was far too sophisticated a chemist to make such a mistake, a fact that is quite evident from the passage I quote below from his textbook, The Principles of Chemistry.

> Notwithstanding the resemblance in the atomic composition of the cuprous compounds, CuX, and the silver compounds, AgX, with the compound of the alkali metals, KX, NaX, there is a considerable degree of difference between these two series of elements. The difference is clearly seen in the fact that the alkali metals belong to those elements which combine with extreme facility with oxygen, decompose water, and form the most alkaline bases; whilst silver and copper are oxidised with difficulty, form less energetic oxides, and do not decompose water, even at a rather high temperature; they even displace

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[1] I might just add that any scholar who has worked on the periodic system is well aware of the rather limited value of Posin's highly over-imaginative account of the life of Mendeleev. For example Greenaway's entry on the history of the periodic system in the Encyclopedia Brittanica warns the reader that Posin's book is a "fanciful and romanticized version."

[2] All I can do is to refer Hettema and Kuipers once again to the standard reference on the history of the periodic system, namely Van Spronsen's excellent book which contains diagrams of all the tables I have mentioned.

hydrogen from very few acids. The difference between them is seen in the dissimilarity of the properties of many of the corresponding compounds. Thus cuprous oxide, Cu_2O, and silver oxide Ag_2O are insoluble in water; the cuprous and silver carbonates, chlorides and sulphates are also sparingly soluble in water. The oxides of silver and copper are also readily reduced to the metal. This difference in properties is in intimate relation with that difference in the density of the metals which exist in this case. The alkali metals belong to the lightest, and copper and silver to the heaviest therefore the distance between the molecules in these metals is very dissimilar- it is greater for the former than the latter. From the point of view of the periodic law this difference between copper and silver and such elements of the I group as potassium and rubidium is clearly seen from the fact that copper and silver stand in the middle of *those large periods* (for example, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br) which start with the true metals of the alkalis - that is to say, the analogy and differences between potassium and copper is of the same nature as that between chromium and selenium, or vanadium and arsenic. (Mendeleev 1891, vol. II, pp. 372-3) [my italics].

The reader will also note in passing that Mendeleev explicitly refers to "those large periods," a feature which flatly contradicts Hettema and Kuipers contention that Mendeleev regarded periodicity as unchanging in length. Furthermore, if one considers the periodic tables of other authors during the pioneering days of the periodic table, one arrives at the same conclusion. For example, most of the tables published by Lothar Meyer, Mendeleev's main contemporary, also contain periods of unequal lengths. The reason why I have labored this point is because the main part of the subsequent program of Hettema and Kuipers is predicated on their incorrect distinction between a naïve periodic system which requires unchanging periodicity and the sophisticated version in which a periodicity of eight is just one of many possible values.

3. The Periodic Table in Chemistry

The second section of the recent article by Hettema and Kuipers is titled "The Periodic Table in Chemistry." Here the authors touch very briefly on the history of the periodic system and claim that three important steps had occurred in chemistry which proved fundamental to the construction of the periodic table. These are,

First of all there was a working concept of the chemical elements.

Secondly it was known that all the chemical elements had different masses, even though it was only possible, initially, to ascribe crude relative weights to each of the elements.

Thirdly it was known that some elements had very similar chemical behaviour. (Hettema and Kuipers 2000, p. 287-8)

The authors claim that these criteria proved sufficient for the construction of the Periodic Table. I would like to comment in passing that each of these three points, as stated, contains some truth but also serves to mask the historical situation due to the manner in which it is expressed in the above list. First of all it is by no means clear that there was a common working concept of the chemical elements. It has been claimed for example, that Mendeleev was able to make more progress than others in developing a successful periodic system precisely because he had a different conception of the nature of the elements (Scerri 2000a). In any case I believe the authors owe it to the reader to explain what they might mean by this working concept of the elements which they say was in place. Are they referring to the concept devised by Boyle or Lavoisier or Mendeleev himself?

The second point is only partly correct in that it was indeed recognized, largely as a result of the work of Dalton, that different elements possessed different masses. But this recognition hardly sufficed to allow the periodic system to emerge. The real problem lay in the conflicting schemes which were used to obtain the relative weights of the different elements. This crisis reached such proportions that in 1860 the first ever international chemical conference was convened in Karlsruhe, following which some semblance of order began to emerge. Only then did it become possible for a coherent periodic system to be assembled.

The third point is essentially correct except for the inclusion of the word 'very' in describing the similarities between some of the elements. There are many examples of groups in the periodic table, even among those recognized in the early days of its history, which are in fact rather different. The elements carbon, silicon, germanium, tin and lead serve as good examples. Carbon is a hard, black, non-metal or a gem stone in one of its other allotropes called diamond. Silicon and germanium are both semi-metallic and also semi-conductors of electricity and heat. Tin and lead are examples of metals which have been known since antiquity. These elements cannot really be said to be very similar.

But the objection to "very similar chemical behaviour" being a necessary condition for the establishment has a more profound aspect. Mendeleev is known to have had a rather complex view of the nature of the elements whereby he did not base his periodic system on the similarity of the elements as simple substances but on what he referred to as "basic substances." For example if one were to consider fluorine, chlorine, bromine and iodine one would probably not see any great similarities among them qua "simple substances" since they are two gases, a red liquid and a violet-black solid respectively. The similarity only emerges if one considers the compounds formed by these elements with sodium, for example, and the fact that they all

form crystalline white solids.[3] According to Mendeleev it is the unobservable elements, in the sense of basic substances, rather than the simple substances which can be isolated, that form the basis of the periodic system.

4. Formalization

In the third section of their recent article Hettema and Kuipers develop the machinery which they hope will permit them to discuss the status of the periodic law and whether the periodic law is reduced to modern atomic theory. One step taken involves the assumption of a finite set E, representing the set of chemical elements. I cannot help wondering why they need to assume that the set of all elements will be finite, since there is no experimental indication that we are close to reaching the last of the elements or that this limit is even on the foreseeable horizon. If anything, the news from the laboratories which specialize in the synthesis of superheavy elements has been rather encouraging for those who believe that there are many more elements left to be synthesized (Armbruster, Hessberger 1998). Unless Hettema and Kuipers can adduce some convincing arguments from nuclear physics as to why they believe that the list of elements must necessarily be finite I do not see why they are entitled to make this assumption within their formal scheme.

After outlining five points, which form their definition 1, the authors state that z or atomic number is the only theoretical term. They add to this the claim that "no experimental problems arose in either the measurement of the atomic mass function m or the chemical similarity function ~ which also feature in their definition. Unless the authors are attributing a highly specific and unexplained meaning to these claims it is difficult to agree with them. There were in fact many severe problems associated with the definition and measurement of atomic weights. As I mentioned above, in passing, this was the main reason why the development of the periodic table was delayed until the late 1860s even though the other "sufficient conditions," as they are termed by the authors, were already in place by the beginning of the nineteenth century. In addition, to claim that chemical similarity could be established with "no experimental problems" is simply incorrect.[4] There are many cases of elements whose properties were very well known and which had been isolated

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[3] I have carried out this fairly detailed analysis of the phrase "very similar chemical behavior" because it is one which recurs frequently in the recent article by Hettema and Kuipers.

[4] The further claim by Hettema and Kuipers is that the measurement of *m* was possible by making use of the "ideal gas law". Although this was true of some elements, not all elements can be easily vaporized with the result that their atomic weight remained undetermined, or mistaken, until another method was devised by Dulong and Petit and quite a different technique by Mitscherlich.

in adequate amounts but whose chemical similarities remained ambiguous for long periods of time.

5. Beryllium

The case of the placement of beryllium is a historically significant one because it involved a controversy that lasted a considerable period of time. The question was whether the element should be assigned a valency of 2 or 3 that would affect its atomic weight and it would, in turn, govern the position it took up in the periodic table.

In the case of metallic elements, Cannizzaro's method for determining atomic weights was not easy to apply, as it required volatile compounds. Instead, other methods such as one based on Dulong and Petit's law of atomic heats continued to be used. Furthermore, the chemical characteristics of the oxides generally provided an indication of the valency of the metal concerned. These rules are summarized below.

low valency oxides	MO & MO_2	strongly basic
intermediate valency oxides	M_2O_3	weakly basic
high valency oxides	MO_2, M_2O_5, MO_3	acidic

The metal beryllium provided one of the most severe tests for Mendeleev's system. The question was whether to place beryllium in group II above magnesium or in group III above aluminum. Its measured specific heat of 0.4079 indicated an atomic weight of approximately 14, which would place beryllium in the same group as the tri-valent aluminum. Furthermore, beryllium oxide is weakly basic, the lattice structure of the metal is unlike that of magnesium and beryllium chloride is volatile just like aluminum chloride. Taking these facts together, the association of beryllium with aluminum appears to be compelling.

In spite of all this evidence Mendeleev supported the view that beryllium is di-valent using arguments which were purely chemical, as well as arguments based on the periodic system. He pointed out that beryllium sulfate presents a greater similarity to magnesium sulfate than to aluminum sulfate and that whereas the analogues of aluminum form alums, beryllium fails to do so. He argued that if the atomic weight of beryllium were 14, it would not find a place in the periodic system. Mendeleev noted that such an atomic weight would place beryllium near to nitrogen where it should show distinctly acidic properties as well as having higher oxides of the type Be_2O_5 and BeO_3 which is not the case. Instead Mendeleev argued that the atomic weight of beryllium

might be approximately 9, which would place it between lithium (7) and boron (11) in the periodic table.

In 1885 the issue was conclusively settled in favor of Mendeleev by measurements of the specific heat of beryllium at elevated temperatures. These experiments pointed to an atomic weight of 9.0 in reasonable agreement with Dulong and Petit's law and supported the di-valency of the element. The difficulties involved in this case, and others like it, demonstrate that chemical similarity is far from a trivial matter to establish.

### 6. The Placement of Lutetium and Lawrencium in the Periodic Table

The case that will be examined in this section involves a change to the periodic classification that has only been carried out in the last twenty years and, which to judge from the vast majority of chemistry and physics textbooks, has yet to be widely assimilated. The debate is over which two elements, both lanthanum and actinium or both lutetium and lawrencium should be placed under scandium and yttrium in group 3 of the periodic table.[5] A considerable amount of physical and chemical evidence has now been established to show quite convincingly that the more correct placement implies that group 3 consists of scandium, yttrium, lutetium and lawrencium.

Until relatively recently the use of electronic configurations dictated that the elements lanthanum and actinium should appear in these positions instead of lutetium and lawrencium. In order to appreciate this situation the electronic configurations which were formerly supposed to occur in the atoms of ytterbium (atomic number 70) as well as lutetium (atomic number 71) must be considered.

Ytterbium   Yb   [Xe] $4f^{13} 5d^1 6s^2$
Lutetium   Lu   [Xe] $4f^{14} 5d^1 6s^2$
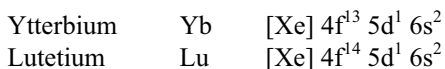
According to this assignment the differentiating electron, that is the final electron to enter the atom of lutetium, is regarded as an *f* electron. This suggests that lutetium should be the final element in the first row of the rare earth elements, in which *f* electrons are progressively filled, and not a transition element as had previously been believed by chemists.

As a result of more recent spectroscopic experiments, however, the configuration of ytterbium has been altered to (Jensen, 1982).

Ytterbium   Yb   [Xe] $4f^{14} 5d^0 6s^2$

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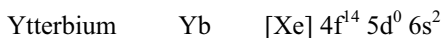
[5] The IUPAC numbering scheme for the groups of the periodic table, which run from 1 to 18, has been used. The older systems denote this as group IIIB in the US and group IIIA in Europe.

while that of lutetium remains unchanged. Ytterbium therefore now appears to mark the end of the rare earths. The subsequent element lutetium shows a differentiating electron labeled d, spectroscopically, which makes it an equally good candidate as lanthanum, of configuration [Xe] $5d^1 6s^2$, for the role of the first element in the third transition series.

Renewed chemical and physical measurements have shown conclusively that lutetium rather than lanthanum bears a close similarity with scandium and yttrium (Jensen 1982). Here then is another example that clearly shows some rather difficult experimental problems concerning the placement of the elements in the periodic system. The statement by Hettema and Kuipers that chemical similarity can be established without experimental problems is patently false, especially as such problems have persisted up to the present time. Moreover, the above mentioned reassignment of lutetium and lawrencium is by no means universally accepted even at the time of writing (Nelson 1996).[6]

7. The Periodic Law

I return to the article by Hettema and Kuipers in order to consider the next section which is entitled "The Periodic Law." Here it is stated that the naïve version of the periodic law (NPL) is due to Mendeleev and that the present-day (sophisticated) one (SPL) was developed in the early 1900s. However neither at this point nor anywhere else do the authors explain precisely what they take to be the developments which underlie what they term the sophisticated periodic law although they claim that "SPL has been developed in close contact with Atomic Theory." As I suggested in my previous critique it is rather important for them to address this question since many developments might be held to be responsible for the change.[7] If we accept the authors'

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[6] The reason why most chemistry and physics textbooks have not adopted the new assignments is not because their authors dispute them but simply that they are not aware of them. The popular Internet periodic table pages which are maintained by Mark Winter of Sheffield University does feature the new arrangement of elements in group 3. Web page http://www.webelements.com/index.html.

[7] Hettema and Kuipers have made some response to my question. At one point in their more recent article they attribute the sophisticated periodic law to the work of Niels Bohr. First they state that "the expression $2n^2$ corresponds to the principal quantum number" but then immediately add "It is however not identical to it." In fact none of the possible developments in Atomic Theory which the authors might be alluding to had any influence on the realization that the lengths of periods vary according to the formula $2n^2$. The latter follows entirely from chemical similarities. All that atomic theory provided was successive explanations of the periodicity. The periodicity itself and the points at which it occurs are chemical, and empirical, phenomena.

contention that the sophisticated periodic law is one that embodies the varying lengths of periods, according to the formula $2n^2$ then we can try to identify when such tables came into existence and try to see whether they did indeed follow any theoretical developments. However, this immediately raises a problem since many rather early periodic tables already displayed the characteristic of varying period lengths.

As I mentioned earlier many of the tables of Mendeleev, Lothar Meyer, Newlands, and other discoverers of the periodic system displayed varying period lengths. One of the earliest periodic tables which not only shows varying period lengths but which consists of the now familiar medium-long form of the periodic table, with varying lengths given by the formula $2n^2$, was published by the inorganic chemist Werner in 1905. But Werner's table was developed quite independently of any theoretical developments such as quantum theory or "Atomic Theory" of any kind.[8] The sophisticated form of the periodic table, in the sense of varying periodicity, did not require any input from atomic theory whatsoever but developed from empirical chemical observations regarding chemical similarities.

The authors then discuss what they term "three requirements which have to be included in the definition of the Periodic Table." These requirements are designated as monotomicity, surjection and injection and are directly connected with ordering according to atomic weights, the lack of empty spaces in the table and a one-one relationship between the order of the elements respectively.[9] While accepting that some of these requirements show exceptions in the sense of pair reversals and the existence of isotopes the authors consider that these requirements are nonetheless useful for establishing the relationship between Mendeleev's naïve periodic law and the sophisticated periodic law. The naïve periodic law is formalized as,

(NPL) $e \sim e'$ iff $| z(e) - z(e') |$ is a multiple of 8.

The formalization given to the sophisticated periodic law is more complicated in that it consists of two parts, the second of which itself is comprised of two parts. The conclusion which Hettema and Kuipers reach is that "It is easy to check that SPL reduces to NPL if n is fixed at the value of $n = 2$ (and hence $2n^2 = 8$)." I would like to suggest that this reduction which the authors claim to have established is trivial and that its establishment does not require any formalization of the periodic system. Surely one could simply state that whereas the older periodic tables had envisaged periods of eight elements, the

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[8] A diagram and account of Werner's table can be found in Van Spronsen's book (Van Spronsen 1969, p. 152-154).

[9] This implies that if two elements have the same order number, they are necessarily the same element.

new version now generalized the lengths of periods to any value conforming to the formula $2n^2$ of which 8 is one special case.[10] Why do we require an elaborate formalization in order to establish this trivial connection?

8. The Atomic Theory and the Periodic Table

In the same section the authors draw another distinction which I began to dispute in my earlier critique. Hettema and Kuipers try to distinguish between what they call the chemical and the physical conception of the atom. Although such an argument could be made in principle, I believe that the version proposed by the authors is erroneous. The authors' first attempt at making this distinction takes the form of,

> …for the chemist, an 'atom' is viewed as an inherent part of a molecule, for the physicist, an atom represents first and foremost a nucleus surrounded by a cloud of electrons. The behaviour of the latter is described by quantum mechanics. (Hettema and Kuipers 2000, p. 296)

If such views might ever have distinguished chemist from physicist then I strongly suggest that such differences have ceased to exist since the advent of quantum mechanics into chemistry. Any casual examination of chemistry textbooks will show that modern chemistry is entirely based on the model of the atom as a nucleus surrounded by a cloud of electrons. Moreover it is not just physicists seeking to understand the atom who draw on quantum mechanics. The theory has become an essential part of any elementary high school or undergraduate course in general chemistry, to say nothing of further study and research in chemistry.

Hettema and Kuipers continue by expanding on the claimed distinction between the chemical and physical conceptions of the atom. They claim that chemists are accustomed to using a qualitative version of the physical picture of the atom whose full implications involves the use of quantum mechanics and computation. After citing some of my previous criticisms approvingly,[11] the authors claim that these qualitative versions used by chemists that involve separation of electrons into core and valence shells,

> can be called 'chemical' again since they deal with the functional definition of the atom as part of a molecule. (Hettema and Kuipers 2000, p. 297)

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[10] However, I am disputing this way of characterizing the naïve periodic system.
[11] Hettema and Kuipers cite me as saying, "such explanations are indeed frowned upon by physicists as being of a typically picturesque and naïve kind, typical of chemists." What Hettema and Kuipers may not have realized was that the main culprit I had in mind was precisely the view of certain numbers of electron in particular shells, the model which they devote so much attention to in their articles.

I regret to say that I also propose to dispute this identification. The separation between core and valence electrons is made as much by physicists as it is by chemists. Indeed the highly successful physics sub-discipline of spectroscopy is dominated by the assumption that the outer electrons are responsible for observed spectroscopic transitions (Condon and Shortley 1935). In addition the use of this approximation throughout atomic spectroscopy confirms that it is in no way linked to the definition of an atom as part of a molecule as Hettema and Kuipers claim.

Also, as I tried to emphasize in my earlier comment, chemists are as much concerned with atoms and the properties of pure elements as they are with those of molecules and compounds. A good case in point is the study of the periodic classification of the elements itself. In establishing or studying the periodic system chemists are concerned with atoms and elements. This is regardless of whether they were early pioneers who depended on observable properties or modern chemists who make reference to electron shells and quantum mechanics to make sense of the periodic classification.

Before leaving this section I would like to cite again a paragraph from Hettema and Kuipers for convenience.

> For most chemists, the correct functional definition of an atom is 'part of a molecule' and the most important property of the atom is its chemical valency. For most physicists, an 'atom' is primarily a nucleus surrounded by a cloud of electrons, the latter being described by quantum mechanics. (Hettema and Kuipers 2000, pp. 297)

The implication that chemists do not use quantum mechanics is mistaken. In fact it is well known to science educators that quantum mechanics is made greater use of in courses in chemistry than it is in physics. In physics courses quantum mechanics represents just one of many topics such as electromagnetism, classical mechanics and relativity, whereas in chemistry quantum mechanics is the dominant theory which is used to explain the properties of all forms of matter. While it may be correct to say that chemists use watered-down versions of quantum mechanics it is an exaggeration to imply that they do not really use quantum mechanics at all as the authors seem to be doing here.[12]

As in the claimed distinction between the naïve and the sophisticated periodic laws Hettema and Kuipers proceed to try to establish the relationship between their conception of the chemist's and the physicist's atom. This part of the project begins with the statement that,

> In the chemical picture of the atom for instance, 'chemical similarity' includes 'having the same valency' whereas in the physical picture, 'chemical similarity' can be related to

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[12] This is true even if one accepts the authors' claim that they are merely representing the extreme positions that differentiate chemists from physicists.

similarities in the electronic configurations (in some cases the valence electrons). This means automatically that the concept of valence itself can be related to 'outer electron configuration'. (Hettema and Kuipers 2000, p. 297-8)

But this sense of chemical valency is one that is more characteristic of modern chemists than physicists. It has become one of the main paradigms of modern chemistry that valency is governed by outer electrons. What the authors are describing as the physical conception of valency and the atom is in fact the modern chemical conception. Meanwhile, to attribute such a view to physicists is mistaken, precisely because physicists go well beyond the independent-electron approximation that assumes that we can speak of a particular number of electrons in any particular shell.

This is a central point that I would like to impress upon Hettema and Kuipers since my previous attempt to do so seems to have failed. The view of particular numbers of electrons in shells around the nucleus dates from the Bohr model of 1913 and further developments in 1922. With the advent of the Pauli Exclusion Principle in 1925 it was realized that individual electrons are not in stationary states although the atom as a whole does still possess stationary states. Calculations on the energies of atoms and molecules must necessarily consider the mixing of electronic configurations if they are to recover anywhere near to the experimental energies of such systems. But even such an interpretation of the calculations involves a partial return to the notion of particular numbers of electrons in shells. In fact all talk of electrons in shells is banished in accurate calculations. The physicist goes beyond the orbital approximation of particular electrons in shells around the nucleus. Rather than being characteristic of the physicists conception of the atom the latter interpretation has been bequeathed precisely to the chemist!

Because of these limitations of the independent-electron model the explanation of the periodic system that Hettema and Kuipers claim can be obtained in terms of the number of outer-shell electrons is somewhat approximate. Nevertheless it does give a post facto explanation of the lengths of successive periods and thus of the $2n^2$ rule which was featured earlier.[13] The authors now acknowledge that the explanation is not complete since the electron shells do not fill sequentially as I argued in my earlier critique. But rather than facing the theoretical problems which this feature raises they merely refer the reader to a standard textbook on quantum mechanics. The

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[13] Hettema and Kuipers state that the old quantum theory of Bohr is sufficient to explain the $2n^2$ rule and that the advent of quantum mechanics as developed by Shrödinger and Heisenberg "does not alter this interpretation." In saying this they fail to mention that the crucial step in the understanding of the periodic table in terms of numbers of electrons in shells and quantum numbers was provided by the Pauli Exclusion Principle and his postulation of a fourth quantum number. Without this development the old quantum theory failed to explain the form of the periodic system.

problem is that many textbooks do not acknowledge that the explanation for the periodic system given in terms of quantum numbers is only successful within the limitations of the homely model of electrons in shells.

When faced with the question of the reduction of the periodic table the modern theoretical physicist requires a deeper level of explanation. He or she is more likely to seek a quantitative prediction of some atomic property or other which shows periodicity and whose experimental values may be compared with calculated values. Such a property consists in first ionization energy, for example, and there are indeed good theoretical predictions of ionization energies that can be obtained from quantum mechanics. But this kind of approach requires going beyond the independent-electron approximation, and the associated notion of specific numbers of electrons in shells. Even then some physicists claim that such a reduction is not sufficiently deductive since the Schrödinger equation for each atom must be solved individually for each atom (Ostrovsky 2001). Such *ab initio* quantum chemistry carried out using linear expansions of terms made up of electronic configurations does not provide a general solution for any atom or molecule. The Schrödinger equation for each atom must be solved from first principles using a basis set (linear combination of electronic configurations) which incidentally is still chosen by reference to the Aufbau principle and not deduced from first principles.[14]

A more satisfactory reduction, but still approximate, can be achieved by using density functional theory. In 1926 Thomas proposed treating the electrons in an atom by analogy to a statistical gas of particles. No electron shells are envisaged in this model although electrons may still possess values for angular momentum as they do in the electron shell model. The method was independently rediscovered by Fermi two years later, and is now called the Thomas-Fermi method. For many years it was regarded as a mathematical curiosity without much hope of application since the results it yielded were inferior to those obtained by the method based on electron orbitals or methods based on orbital expansions.

Gradually the Thomas-Fermi method, or its descendants that have become known as density functional theories, has become as powerful as methods based on orbitals and in many cases can outstrip the orbital approaches in terms of computational accuracy (Gill 1998). The reason why these approaches may be considered more genuinely ab initio, or a deeper form of reduction, if I may speak loosely, is that one obtains a global solution for all the atoms in the

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[14] The point I am making here is that although the calculation of the ground state energy of an atom, or its ionization energy, appears to be carried out rigorously from first principles, the choice of the basis set cannot be deduced from first principles. There is a strong sense in which so-called ab initio calculations are not strictly ab initio because of this feature (Scerri 1998, 1999, 2000d).

periodic table and even elements not yet discovered. The solution is expressed in terms of the variable Z which represents atomic number, and is the crucial feature which distinguishes one kind of atom from that of any other element. One does not need to repeat the calculation separately for each atom since the equation is solved once and for all for all possible atoms.

Incidentally, there is an important conceptual or even philosophical difference between the orbital methods and these density functional methods. It is that in the former case the theoretical entities are as a matter of principle completely unobservable whereas electron density invoked by density functional theories is a genuine observable. Experiments to observe electron densities have been routinely conducted since the development of X-ray and other diffraction techniques (Coppens 1997). This is why I and some others have been agitating about the recent reports, starting in Nature magazine in September 1999, that atomic orbitals had been directly observed (Scerri 2000b). This is simply impossible. Orbitals cannot be observed either directly, indirectly or in any other way since they have no physical reality. This state of affairs is dictated by quantum mechanics. Electron density is altogether different, as I have indicated, since it is a genuine quantum mechanical observable. I have tried to stress the educational implications of the claims for the observation of orbitals in other articles and will not dwell on the issue here (Scerri 2000c).[15]

9. A Case of Reduction

Hettema and Kuipers further claim that the case of the periodic table, concerning the relationship between the naïve and sophisticated versions, can be considered as an interesting case of a reductive explanation or reduction for short. They draw upon an account of explanation that requires what they term aggregation, identification and approximation. On the question of identification the authors state that,

> The necessary link between chemical similarity and 'equal outer electron configuration' states that the latter causes the former (Hettema and Kuipers 2000, p. 300).

This is a point which I touched on in my earlier critique but which I need to emphasize further. As I stated before the possession of any particular electronic configuration by an element is neither necessary nor sufficient for chemical similarity with another element. It is rather easy to generate counter

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[15] Indeed as time has passed the best of both approaches have been blended together. Many computations are now performed by a careful mixture of the orbital and density functional approaches that are used within the same calculation scheme.

examples that show quite convincingly the lack of necessity or sufficiency. The element helium has two outer-shell electrons that might lead one to think that it would necessarily be similar to alkaline earth elements such as calcium or magnesium. In fact nothing could be further from the truth since helium is the single least reactive element in the entire periodic system while magnesium and calcium are reactive metals.[16] One need only consider the vigorous reaction that occurs when a few calcium pieces are placed into a beaker containing water. So much for sufficiency.

Similarly the hope of any necessary connection which the authors believe exists also suffers from serious counter examples. The elements nickel, palladium and platinum are placed in the same column of the periodic table, namely group 10, because of their close chemical similarities. However no two elements within this group of three share the same electronic configurations in its two outermost orbitals. They are respectively, Ni $3d^8 4s^2$; Pd $4d^{10} 5s^0$; Pt $5d^9 6s^1$. Of course this is quite apart from the problems alluded to earlier concerning exactly what is meant by chemical similarity. There is no clear-cut notion of this concept in chemistry as shown by the difficulties in the placement of certain elements such as beryllium, lawrencium and lutetium into the periodic system.

10. Is the Periodic Table a True Theory?

Hettema and Kuipers begin the section with the above sub-title by conceding that,[17]

> Most books on the subject of practical chemistry treat the Periodic Table as a *table*, and do not mention the word theory. (Hettema and Kuipers 2000, p. 300)

But they go on to propose that in fact the naïve version of the periodic table associated with Mendeleev's table should be regarded as a theory and that the sophisticated periodic law must be regarded as an empirical law because of the explanation which is provided by atomic theory. The basis of this claim seems to be the particular analysis that the authors have utilized concerning the "proper theories" and "empirical laws" and the relationship between them.

> A theory is a proper theory if it has at least one T-theoretical term. It is an empirical law (in the strict sense) if it has none. Hence an empirical law is an improper theory, i.e. a theory without theoretical terms of its own (Hettema and Kuipers 2000, p. 301).

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[16] The only similarity might be the observed pattern of splitting of spectral lines in the presence of a magnetic field. However this can by no means be referred to as a chemical similarity.

[17] The authors would have been more correct in saying that there is not a single example of any book or article, either in chemistry or philosophy of science, apart from their own work, which has ever suggested that the periodic table should be regarded as a theory.

The crucial term that the authors take to distinguish Mendeleev's periodic table from the sophisticated version is atomic number. The authors claim that Mendeleev used atomic number implicitly while it still had no experimental underpinning and could therefore be regarded as a theoretical notion. The presence of this alleged theoretical term is thus taken to render Mendeleev's table, or the naïve periodic table, into a theory. By contrast the sophisticated periodic table also draws on atomic number as the ordering principle. But because of the theoretical account that is provided by atomic theory, Hettema and Kuipers conclude that atomic number is no longer a theoretical term. It follows in their view that the sophisticated periodic table cannot be regarded as a theory but must be regarded as an empirical law.

I see at least one major flaw in this way of looking at the periodic table. I believe that the assumption that Mendeleev used atomic number implicitly cannot be sustained. What he used, as is well known, was atomic weight. The fact that atomic weight and atomic number are well correlated throughout the periodic system does not allow one to make the identification which Hettema and Kuipers wish to make. The use of atomic number has the virtue of solving the problem of remaining gaps in the periodic system in a definitive manner. Once Moseley had carried out his famous X-ray experiments it became possible to determine precisely which elements remained to be discovered or where any remaining gaps existed in the periodic table. However, Mendeleev and other pioneers of the early periodic system did not share this luxury. They had the difficulty of trying to estimate where any gaps might lie and where to place the known elements within columns of the table. What renders this task particularly difficult is that the increase in atomic weights of the elements is far from regular.

This can be illustrated by considering the values of the atomic weights of the first row of the rare earth elements for example.[18]

La	Ce	Pr	Nd	Pm	Sm	Eu	
138.9	140.1	140,9	144.2	(145)	150.4	152.0	
Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
157.3	158.9	162.5	164.9	167.3	168.9	173.0	175.0

Rather than a smooth progression in atomic weights one notices a virtual twinning of elements by increasing atomic weights. It is mainly because of the irregularity in the gaps between their atomic weights that the rare earths proved to be so difficult to place in the periodic system. But even when some

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[18] Modern values of atomic weights are used and rounded to one decimal place. The value in parentheses refers to the weight of the most stable isotope of the element.

of these atomic weights became available it was not possible to infer which elements were still missing, a feat that only became possible following the discovery of atomic number. It is therefore rather far-fetched to claim that Mendeleev implicitly used atomic number as an ordering scheme.

As a matter of historical fact, the only pioneer of the periodic system who might be said to have anticipated atomic number was John Newlands, who did not receive much credit for his published periodic systems. Nevertheless, his use of ordinal number, rather than values of atomic weight, did not allow him to produce better periodic systems than his contemporaries. Just like Mendeleev, and others who worked with atomic weight, Newlands did not know what gaps to leave. Of course the ordinal numbers that he associated with successive elements, which were known at the time, do not correspond with the modern atomic numbers that are given by the number of protons in the nuclei of the various atoms in question.[19]

In the same section of their paper Hettema and Kuipers claim that

> ...Mendeleev was willing to admit that global satisfaction of the naïve empirical claim at least required acceptance of some local exceptions (Hettema and Kuipers 2000, p. 302).

This is unfortunately not quite the case although a view that is propagated by many textbooks on chemistry. Although Mendeleev reversed the elements iodine or that of tellurium on chemical grounds he did not consider these to be exceptions to the ordering principle of increasing atomic weights. Mendeleev maintained throughout his life that either the atomic weight of iodine or that of tellurium had been incorrectly determined and encouraged experimenters to re-determine the weights of these two elements. But despite strenuous efforts, on the part of many chemists, the order in the atomic weights of these two elements remained unchanged. Tellurium does indeed have a higher atomic weight and yet must be placed before iodine on chemical grounds. Whereas Mendeleev repeatedly stressed that there would be no exceptions to the ordering of elements according to strictly increasing atomic weights the subsequent discovery of ordering based on atomic numbers has shown that he was incorrect.[20]

11. Conclusion

After devoting so much space to criticizing the views of Hettema and Kuipers I would like to conclude by saying that they are to be applauded for undertaking

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[19] The view that Newlands, in some sense, anticipated atomic numbers is not universally accepted and has been recently disputed by Giunta (1999).

[20] It is now known that tellurium is correctly placed before iodine because it has one fewer protons in the nuclei of its atoms. The lower atomic weight of iodine atoms is due to the fact that most common isotopes possesses fewer neutrons than the most common isotopes of tellurium.

the very difficult problem of the reduction of chemistry. Whereas one frequently hears complaints that chemistry has been sadly neglected in philosophy of science I believe that this situation is as much due to the difficulty of the problems it presents rather than mere avoidance on the part of philosophers. I hope that my comments will spur Hettema and Kuipers and others to renewed attempts towards the reduction of the periodic system. As Popper once wrote, reduction is not always successful but attempts to carry it through invariably deepen our knowledge of the phenomena concerned in unexpected ways (Popper 1974).

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